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THE ELEMENTS

OF

PHYSICAL CHEMISTRY

BY

J. LIVINGSTON R. MORGAN, PH.D.,

Professor of Physical Chemistry in Columbia University.

FOURTH EDITION, REVISED AND ENLARGED.

FIRST THOUSAND.

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PREFACE TO THE FIRST EDITION.

THE object of this book is to present the elements of the entire subject of Physical Chemistry in one volume, together with the important and but little known applications of it to the other branches of chemistry. Many persons have found it difficult to obtain a comprehensive outline of the subject, owing to the length of time which it has been necessary to spend upon the separate volumes devoted to special portions of it. To all such this volume may be of value.

It is especially intended as a text-book for either class-work or self-instruction, and although the calculus is used in the derivation of some of the laws, still much can be done without any training in the higher mathematics. In general, references are given, so that any one wishing to make an extended study of any special portion may do so with little difficulty. The amount of the subject included, however, embraces that which is likely to be useful to all chemists, and is that wh is being given to all chemical students at Columbia University.

No claims of originality are made for the major portion of the text, for Ostwald's Lehrbuch der allgemeinen Chemie and Analytical Chemistry, as well as Le Blanc's Electrochemistry and Nernst's Theoretical Chemistry, have been very freely used. Some things, however, will be found in a new form, which it is hoped is simpler and clearer than the usual one.

The arrangement as well as the scope of the volume is new, which I think makes the subject more logical and clear.

J. L. R. M.

DEPARTMENT OF PHYSICAL CHEMISTRY,
HAVEMEYER LABORATORY,
COLUMBIA UNIVERSITY,
December, 1898.

PREFACE TO THE SECOND EDITION.

In preparing this edition, I have endeavored to do three things: first, to bring the subject-matter itself up to date; second, to make, wherever possible, the relations clearer than before; and third, to render the book itself more useful to those studying the subject without an instructor. The physical meaning of all relations is shown, so that those who have not sufficient mathematical training to actually derive the single relations will at least understand them and be able to apply them when necessary. Many things found superfluous in the old edition have been omitted and a number of new relations added. Following the advice of Prof. Ostwald, the chapter on the rôle of the ions in analytical chemistry has been given a place in Chapter VII between chemical equilibrium and kinetics. In Chapter X a collection of problems is given which will show the value and application of each important relation considered. This collection, I think, will be particularly acceptable to those studying alone, as well as to others who have already studied the subject but not yet attempted to apply it.

J. L. R. M.

HAVEMEYER LABORATORIES,
December, 1901.

PREFACE TO THE THIRD EDITION.

As a basis for the revision of this work I have been so fortunate as to have a copy of the former edition containing suggestions and criticisms from the hand of Prof. Ostwald. For his great kindness in having volunteered to take this trouble, and for many other favors, both during my student days and since, I am indeed very grateful, and I cannot allow this opportunity to pass without expressing to him, as far as words may suffice, my sincerest thanks. Further, I wish to acknowledge the influence of his "Vorlesungen über Naturphilosophie," some points of which I have attempted to apply in this edition.

The ideas I have had in mind in making this revision may be summarized as follows: To bring the subject-matter up to date; to distinguish sharply between hypothesis and fact, avoiding the former as far as is possible; and to accentuate the physical meaning of the results of mathematical reasoning, i.e., to employ mathematics simply as a means to an end, and to make the matter as intelligible as possible, even to the non-mathematical reader. In few words the motive, if I may so express myself, of this edition is to treat the subject as something which can be applied to other branches and to illustrate the application and methods of application by the use of numerous problems. In this way it is hoped that the subject, instead of being merely a more or less interesting theoretical study, as is too often the case, may appeal to the student as a tool by the aid of which *actual results* may be obtained. This plan is the expression of the need of my own students, and I assume consequently that it will be welcome to others who not only wish to *know* the subject, but also to *use* it.

J. L. R. M.

COLUMBIA UNIVERSITY,
May, 1905.

PREFACE TO THE FOURTH EDITION.

All the changes made in this edition have been undertaken with the view of bringing the subject-matter up to date and making the various relations more intelligible to the average, non-mathematical, reader. To this end, and to retain the approximate size of the volume, the more unnecessary portions of the other editions have been omitted, and in all cases the physical meaning of the derived relations has been given immediately after the derivation, in order that those who cannot follow the derivation may at least be able to use in practice the results obtained from it. The sections on "indicators" and "general analytical reactions" have been omitted, for they are now presented in all the better text-books on analytical chemistry.

J. L. R. M.

Columbia University,
June, 1908.

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ELEMENTS OF PHYSICAL CHEMISTRY.

CHAPTER I.

INTRODUCTORY REMARKS.

1. **Physical Chemistry** *is that branch of the science of chemistry which has for its object the study of the laws governing chemical phenomena.*

Other titles for this subject are also in use (General Chemistry, Theoretical Chemistry), but, since the subjects treated lie in that border-land between Physics and Chemistry, and since many purely physical methods are used, the term Physical Chemistry is the most descriptive one, and is to be preferred. The subject of Physical Chemistry is usually divided into two parts: Stoichiometry and Chemical Energy, the latter term including the laws of affinity and all other allied subjects. As it is difficult, however, to make a sharp distinction, we shall consider both together, dividing the subject only into minor portions in the form of chapters.

2. Energy.—Since much of our work has to do with the different forms of energy, it will be well first to recall some points which later we shall use constantly.

Force is whatever changes, or tends to change, the motion of a body by altering its direction or its magnitude. The unit of force is the dyne. A dyne acting upon a gram for one second will give it the velocity of 1 centimeter per second, and *n* dynes, *n* centimeters per second. At Washington a body falling freely for one second acquires the velocity of 980.10 centimeters, therefore the force of gravitation of 1 gram at Washington is equal to 980.1 dynes.

Work.—The unit of work is that work which is done when unit force is overcome through unit distance. This is called the erg. We have then

$$\text{dynes} \times \text{centimeters} = \text{ergs}.$$

The maximum work to be obtained from any process is that amount which can be produced under ideal conditions.

Energy is work or anything which can be transformed into work, or produced from work.* Mechanical energy is of two kinds, kinetic and distance—the former being due to motion, the latter to position. As all forms of energy can be transformed the one into the other, the general unit of energy is the erg. Since it is impossible to remove all the energy from a body, we have no way of determining how much is contained in it. We can only measure the excess of energy which a body contains in a given state over that which it contains in a certain standard state. This is determined by allowing a body to go from the given state to the standard state in such a way that the difference in energy all appears in a measurable form, for example, as heat. If we measure this heat, we have the energy of the body in the given state, as compared to that in the normal state.

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* See Oswald's Vorlesungen über Naturphilosophie. Second edition p. 158.

3. **Atomic and Molecular Weights.**—Since we are to make very extensive use of these two factors in our later work, it is quite necessary here to make clear the exact meaning of the words, as we shall employ them. A glance at the practical application of the concepts shows that there is nothing hypothetical about them, other than the derivation of the words. It is unfortunately true, however, that from this one early acquires the idea that the actual results of an analysis or chemical reaction are dependent not only upon the *practical work*, but also upon the *molecular* or *atomic hypothesis*. This idea is so strong, indeed, that it is not uncommon to find people assuming that any direct proof contrary to the hypotheses would actually affect the practical results themselves. It is not possible to discuss this question in detail here, so the

reader must be referred elsewhere.* The definition of the two terms, however, will serve to show that they are simply expressions of experimentally determined facts, and in such a sense they are used throughout this book.

In order that a similar confusion may be avoided with the other concepts, which are introduced later in our work, we shall always *define each concept in terms of experiment*, for then there can be no question as to whether it is hypothetical (susceptible to neither proof nor disproof), or a fact, a theory which can be proven or disproven by further experiments, or a law which has been proven by past experiments.

The *molecular* or *formula weight* in the gaseous state (that in other states will be defined later) expresses the number of units of weight of gas which at 0° C. and 1 atmosphere pressure occupy the same volume as 32 units of weight of oxygen, or 2 units of weight of hydrogen; i.e., approximately 22.4 liters (see p. 9) when the unit of weight is taken as the gram, or a corresponding volume at any other temperature or pressure. Since the factor for the conversion of grams into ounces (av.) (0.0353) is the same as that for the conversion of liters into cubic feet, this relation also holds for ounces (av.) and cubic feet. In other words, the molecular weight of any gas, expressed in ounces (av.), occupies the volume of 22.4 cubic feet at 0° and 1 atmosphere pressure.

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* See Ostwald, l. c.

The *atomic* or *combining weight* of any element is the weight which combines with 16 units of weight of oxygen, or some multiple or submultiple of that; or combines with the combining weight of some other element, the value of which is expressed in terms of oxygen. Or is the weight which combines with 1 gram of hydrogen, or some multiple of it.

A much simpler definition of atomic or combining weight, applicable to the states in which the molecular or formula weight can be determined by direct experiment, is the following: *The atomic or combining weight is the smallest weight of an element which is found to exist in the molecular or formula weight of any compound.*

CHAPTER II.

THE GASEOUS STATE.

4. Definition of a gas.—A gas is distinguished by its property of indefinite expansion. In other words, a gas is limited in volume only by the walls of the vessel which contains it.

5. The gas laws.—These are the result of experience as to the behavior of gases in general under varying conditions.

Boyle's (Mariotte's) law: At constant temperature the volume of any gas is inversely proportional to the pressure under which it exists.

If v represents the volume of any weight of a gas at the pressure p, and v_1 the volume of the same amount of the gas at the pressure p_1, then

$$pv = p_1v_1 = \text{constant for constant temperature.}$$

If the temperature is different for the two cases the product pv is no longer equal to the product p_1v_1.

The effect of a change in temperature upon the volume of a gas is given by the *law of Charles (Dalton, Gay-Lussac)*; *The volume of any gas increases by the*

1/273 part of its volume at 0° C. for every increase of its temperature equal to 1° C.

If the temperature were decreased continuously from 0°, we would finally reach a point at which the volume is equal to zero. Provided that the law of Charles holds for such a low temperature, this point will be 273 centigrade degrees below 0° C. This point is called the *absolute zero*, and the temperature measured from it in centigrade degrees is the *absolute temperature*. This is designated by the letter T, the temperature according to the centigrade scale being distinguished by the letter t. Between these two terms, then, we have the relation

$$T = t + 273, \quad \text{or} \quad t = T - 273.$$

The volume of a gas is thus proportional to its absolute temperature, provided its pressure remains constant; and, by Boyles' law, its pressure is proportional to the absolute temperature, when its volume remains constant. From this we can now find the value of the product pv for any temperature. We have

$$v \propto T (p = \text{const.}),$$

$$v \propto \frac{1}{p} (T = \text{const.});$$

hence

$$v \propto \frac{T}{p}$$

and

$$v=k\frac{T}{p}$$

or

$$pv=kT.$$

But at 0° C.

$$p_0v_0=k273,$$

and combining these two equations, with elimination of the constant k, we find

$$pv=\frac{p_0v_0}{273}T.$$

This term $\frac{p_0v_0}{273}$ is a constant for any one gas, however, for $p_0=1033$ grams per square centimeter (i.e., 76×13.59) and v_0 is the volume occupied by a definite weight of the gas under this pressure at the temperature of 0° C.

If v_0 is the volume of 1 gram of gas at 0°, 76 cms., we have

$$pv=rT\left(\text{i.e., }\frac{p_0v_0}{273}\text{ for 1 gr.}=r\right),$$

where v is the volume of 1 gram of gas at the temperature T and the pressure p, and r is the *specific gas constant of the gas.*

Or, comparing such quantities of different gases as will give the volume of 22.4 liters at 0° C. and 1 atmosphere pressure (i.e., comparing the molecular weights), we find

$$(1) \qquad pV = RT\left(\text{i.e., } \frac{p_0 v_0}{273} \text{ for 1 mole* } = R\right),$$

where R is the *molecular gas constant,* which is the same for all gases. r multiplied by the molecular weight of the gas, then, must be equal to R, for $Mv = V$ and consequently $Mr = R$; i.e., r is inversely proportional to the molecular weight of the gas.

Equation (1) is the *equation of state for gases.* In it p, the pressure, is to be expressed as a weight in grams upon the square centimeter, V is the volume of one mole in cubic centimeters, and T is the absolute temperature in centigrade degrees, i.e., $T = t + 273°$.

The molecular gas constant, R, which is an energy quantity, since p times V represents work, and T is a pure number, may be calculated as follows:

In $R = \frac{p_0 V_0}{273}$, $V_0 = 22400$ cc., hence $R = \frac{22400 \times 1033}{273}$ $= 84800$ gram centimeters, where the weight of 1 gram per square centimeter is taken as the unit of pressure. To transform this into absolute units it is then only necessary to multiply it by 980.1 (page 2).

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* From here on we shall call the molecular weight in grams the mole, as has been proposed by Prof. Ostwald. A mole of any gas at 0° and 76 cms. pressure occupies 22.4 liters, which is the average result of many determinations on different gases.

Or, if p_0 is given in atmospheres and V_0 in liters, we have

$$R=\frac{p_0V_0}{T}=\frac{22.4}{273}=0.0821 \text{ liter-atmospheres,}$$

a liter-atmosphere being the work done by 1 atmosphere on a square decimeter through a decimeter; and $R=\frac{p_0V_0}{T}=8.31\times10^7$ ergs, when p is given in dynes and V in cc.

If the gas is formed from a solid or liquid, i.e., transformed from a negligibly small volume to the volume it occupies as a gas at p and T, V in equation (1) will be the increase in volume, and pV (i.e., $p\Delta V$) will express the external work done when 1 mole of the gas is formed from negligible volume. We shall have then

$$p\Delta V=RT,$$

and since, so long as the gas laws hold, pressure and volume at constant temperature will be inversely proportional, RT will always have the same value for one mole at any one temperature, independent of the pressure. We can always use the RT side of the equation, then, to express the work, and need not first find the volume at the required pressure and then their product, for although an infinite number of volumes would be possible, depending on the pressure, the product of p and ΔV would always be the same at T, and equal to RT. In addition to the definition of molecular or formula weight, as a gas, already given, i.e., *the weight occupying the same volume as 32 grams of oxygen, or 1 gram of hydrogen, under like conditions of pressure and temperature*, we have, then, the following: *The molecular or formula weight of a substance in the gaseous state is that weight which, in being formed from negligible volume at any temperature T against any pressure, does the external work RT.*

Since equation (1) for n moles would lead to nRT, so here the work of forming n moles would naturally be nRT. The units in which it is expressed being dependent upon the one selected for the expression of R (gram-centimeters, calories, liter-atmospheres, ergs etc.).

In calculating either p, v, or T, when the other two are known, we can make use of equation (1), or of the simple proportions:

$$v_1:v_2::p_2:p_1 \quad \text{(const. } T)$$
$$v_1:v_2::T_1:T_2 \quad \text{(const. } p)$$
$$p_1:p_2::T_1:T_2 \quad \text{(const } v).$$

Dalton's law refers to the pressure exerted by the single gases in a mixture of gases.

The pressure exerted upon the walls of a vessel containing a mixture of gases is equal to the sum of the pres-

sures which the single gases would exert were they alone in the vessel. The exact meaning of this will be seen from the following example: When into a closed exhausted vessel we introduce 1 gram of gas it will exert a certain pressure upon each square centimeter of the surface. If now we introduce a second gram of the same or a different gas, it will exert exactly the same pressure upon the vessel that it would have exerted had the first gram not been there. Upon the walls, however, *with the same gas,* the pressure will be doubled.

One law still remains to be considered which has had and still has great value in chemistry; it is *Avogadro's law: All gases under the same conditions of pressure and temperature contain in unit volume the same number of moles.* In its original form this relation referred to the hypothetical molecules themselves (not to gram molecules, i.e., moles), and hence was hypothetical. In the form given above, however, it is simply expressive of the definition of molecular weight already given (pp. 4, 9, and 11). As a matter of fact the original form has always been used of late as though it did refer to gram molecules, so that the hypothetical character has been lost, and the relation may well be designated as *Avogadro's law.*

By determining the density of any gas referred to oxygen it is very easy, then, to determine its molcular or formula weight. Since equal volumes under like conditions contain the same number of moles, the weights of these volumes will be related as the molecular weights, the basis of which is that of oxygen, i.e., 32. The term formula weight, which we shall use as identical with molecular weight, is to be preferred to the latter, for the formula shows distinctly the relation between atomic weight (i.e., the combining weight) and molecular weight (i.e., the sum of the combining or atomic weights which occupy the volume of 22.4 liters at 0° C. and 760 mm. Hg pressure). Thus H represents the atomic weight of hydrogen (i.e., 1.008, based on $O = 16$), while H_2 is the molecular or formula weight (i.e., 2×1.008 gr.); and for compounds this is much more convenient, especially since the molecular or formula weight is not a fixed quantity for all conditions, but varies with these. Thus we have $FeCl_3$ and Fe_2Cl_6, according to the conditions, and a glance at the formula shows at once the molecular weight.

6. The specific gravity of gases.—The specific gravity of a gas is the weight of the unit of volume, but as this is always very small it is customary to find in these terms the value of a certain gas taken as a standard, and then to express the density of other gases in terms of this gas, taken as unity.

As the composition of air varies, oxygen has been chosen as the chemical standard. Since this is very easily obtained in the pure state and its combining weight with other elements can be accurately determined, its advantages as a standard are apparent.

One liter of O weighs 1.4290 grams at 0° and 76 centimeters pressure. Its specific volume, i.e., the volume of 1 gram. at any temperature and pressure, is

$$v=\frac{p_0v_0}{p}\cdot\frac{T}{273}\text{ cc.}$$

(from the proportions,

$$v:v_0::p_0:p,$$

and $$v:v_0::T:T_0,$$

where $$T_0=273^\circ,\text{ i.e., }0^\circ\text{ C.})$$

$$v=\frac{1}{0.001429}\cdot\frac{76}{p}\cdot\frac{T}{273}=699.8\,\frac{76T}{273p}\text{ cc.}$$

Its density, i.e., the weight of 1 cc., at any temperature and pressure, is the reciprocal of the specific volume, i.e.,

$$d=\frac{1}{v}=0.001429\cdot\frac{273p}{76T}\text{ grams}$$

The molecular volume, since $O_2=32$, is

$$V=32\times699.8\,\frac{76T}{273p}\text{ liters.}$$

If w is the weight of a gas, and g is the weight of an equal volume, under like conditions, of the standard gas, i.e., O, the specific gravity of the gas is

$$s=\frac{w}{g}.$$

The relation in weight between hydrogen and oxygen is as 1:15.88; between hydrogen and air is as 1:14.48. In this way knowing the density referred to one, that referring to either of the others can be determined. Referred to air the density can be employed to find the molecular weight by aid of the formula

$$M=0.001293\times 22400\Delta=28.96\Delta,$$

where 0.001293 is the weight of 1 cc. of air at 0° and 76 cm. pressure, and Δ is the density of the gas based upon air as a standard.

Since by definition the molecular weight in the gaseous state is the weight of a definite volume under standard conditions, molecular weights must be related as the densities of the gases, i.e., as the weights of unit volume. We have then

$$M_1:d_1::M_2:d_2::M_3:d_3, \text{ etc.};$$

or,

$$M_1=\frac{d_1M_2}{d_2}=\frac{d_1M_3}{d_3}, \text{ etc.};$$

and if the density of the gas 2 (or gas 3) is taken as unity, and the other densities expressed in terms of this we have

$$M_1 = d_{12}M_2 = d_{13}M_3,$$

where d_{12} is the density of gas 1 in terms of 2, and d_{13} is the density of gas 1 in terms of 3. In other words, *the molecular weight of any gas is equal to the product of its density referred to a standard gas, into the molecular weight of the standard gas.*

Thus the molecular weight of any gas is twice its density referred to hydrogen; thirty-two times its density referred to oxygen, and twenty-eight times its density referred to nitrogen; for 2, 32, and 28 are the molecular weights of H, O, and N.

7. Methods of determining the specific gravity.—Here we shall consider the subject both for gases and for the vapors generated from substances by heat, since the determination of the latter is of importance for the ascertaining of the molecular weight. For convenience we shall divide the subject into three groups of methods, but shall consider only the theory of the methods, assuming that the student will look up the practical details in one of the many laboratory manuals. (See Findlay's "Practical Physical Chemistry," for example.)

A. The weight of a certain volume of the gas.—This may be used both for gases and for the vapors given off by substances under high temperatures.

α. *For gases.*—The weight of a certain volume is found by weighing first a balloon filled with the gas, and then exhausting this and weighing it alone. In this way we can find the weight of the volume of gas, and by comparing this with the weight of the same volume of oxygen ascertain the density.

β. *For gases generated from substances by heat* (Dumas).—Here the process is slightly different. The substance is placed in a weighed flask with a slender neck and the whole heated at a constant temperature until the substance is all transformed into gas, when the neck of the flask is fused together. After cooling, the flask is weighed and the neck cut off so that the volume of the flask can be found from the weight of water it will contain. We have then the weight of a certain number of cubic centimeters of the gas, which, when compared with the weight of an equal volume of oxygen at that temperature, will give the density referred to that gas, and then by calculation that based upon hydrogen or air.

This method of Dumas has been further modified, so that it is possible to work under diminished pressure and consequently at lower temperatures, which is of great importance in case the substance decomposes at a higher temperature. The flask for this purpose is the same as that used before except that the neck is connected with an air-pump and manometer. When the pressure has reached the desired point the temperature is increased until the substance goes into the gaseous form, when, as above, the neck is sealed. The calculation is the same as before except that the pressure under which the gas exists is equal to that of the barometer minus that of the manometer.

B. The volume occupied by a certain weight.—By these methods we avoid the error which is always present when the weight of a volume of gas is determined. The substance, in solid or liquid form, is weighed and then transformed into the gaseous state, the volume which it then occupies being measured. The method of Gay-Lussac, as improved by Hofmann, is intended only for the determination of the specific gravity of the gases formed from solid or liquid substances. A weighed amount of substance is brought into the Torricelli vacuum of a barometer-tube, which is surrounded by a temperature bath, and the volume of the gas measured. The gas is under a pressure equal to that of the atmosphere minus that of the column of mercury in the tube. This volume of gas, reduced to 0° C. and 76 cms. of Hg, weighs just what the original substance did, and this weight compared with that of an equal volume of the standard gas will give the density.

The method of Victor Meyer differs from that of Hofmann in that the gas is formed in a flask and displaces the air, the volume of this at a lower temperature being measured in a burette connected with the flask. This volume is of course the same as that the substance itself would assume at that temperature, provided that no condensation takes place, for the coefficient of expansion of all gases is the same.

The method under this group which may be used for gases in general is to pass a determined volume of the gas over or through a weighed substance which will absorb it all. In this way the difference in weight of the substance before and after the passage of gas gives the weight of the determined volume of gas. Thus oxygen may be absorbed by glowing metallic copper, the copper oxide formed giving the weight of copper plus oxygen.

C. The value of this method (Bunsen's), which is adapted only to gases, is that but very small amounts of substance are needed for the experiment. It depends upon the relation of the velocity of outflow of a gas through a small aperture to the specific gravity of the gas. The formula is derived as follows: Let p be the difference between the pressure under which a gas exists and that of the atmosphere, and v be the volume of the gas which flows out in the unit of time. The total work done by the change in volume is then pv. Since this work is used to force the gas out, it is equal to the increase of kinetic energy of the gas, i.e.,

$$pv = 1/2mc^2,$$

where c is the velocity of outflow of the gas, and m is its mass. If equal volumes of different gases are considered, flowing through the same-sized openings under the same pressure, then

$$pv = 1/2m_1c_1^2, \quad pv = 1/2m_2c_2^2,$$

or

$$c_1 : c_2 :: \sqrt{m_2} : \sqrt{m_1},$$

or, since the masses of equal volumes are proportional to their densities

$$c_1 : c_2 :: \sqrt{d_2} : \sqrt{d_1}.$$

The apparatus used by Bunsen is very simple. A glass tube having a very fine opening at one end, below which is a stop-cock, is clamped into a vessel of mercury. In this tube is a piece of glass rod to act as a float, while on the outside there are two marks close together. The gas is now passed into the tube at a certain pressure, and the tube lowered into the mercury until the float is just at the lower mark. The cock is then opened and the time necessary for the passage of the float from the lower to the upper mark observed. Since the time is inversely proportional to the velocity, we have

$$t_2 : t_1 :: \sqrt{d_2} : \sqrt{d_1}.$$

By carrying out the experiment for one gas and then for oxygen we can find the density of the gas in terms of oxygen. The results by this method, and this is true in a lesser degree for all methods for molecular weight, are not exact, but are simply intended to indicate what number of combining weights of an element, or what weight of a compound, represents the formula weight. For this reason very great accuracy is not necessary, for it is only a question of finding whether the combining weight or the simplest ratio, as found by analysis, is to be multiplied by the factor 1, 2, 3, etc.

8. Abnormal vapor densities. Dissociation. — The specific gravity or density of the gases generated by heat from substances is found in many cases to be too small, i.e., the molecular weights thus determined are smaller than the theoretical values. And, further, the molecular weight is found to vary with the temperature, pressure and some other factors. These results, naturally, must be obtained with greater accuracy than those mentioned above if the process is to be followed at all closely. Since, according to our definition of molecular weight, 1 mole occupies 22.4 liters at 0° and 760 mm. pressure, a smaller density would represent a decomposition of the substance employed. Thus if a substance decomposes in such a way that from each mole of the gas there are two others formed, then the vapor density must be one half what it should be. For each volume of the undecomposed gas we shall have two volumes of the gases formed from it at the same temperature, since by Avogadro's law we have the same number of moles in equal volumes. These two volumes, however, will weigh the same as the original one volume, so that the weight of one volume of the mixed gases will be one half that of one volume of the undecomposed gas. St. Clair Deville called this decomposition *dissociation*. Thus NH_4Cl dissociates according to the scheme

$$NH_4Cl \rightleftarrows NH_3 + HCl,$$

where the sign $\rightleftarrows$ means that the reaction may go in either direction, according to the conditions. That these two gases, NH_3 and HCl, are actually present in the vapor of NH_4Cl can be shown in the following way (Pebal and Than): A lump of solid NH_4Cl is placed in a tube upon an asbestos plug, and the temperature of the tube raised. The NH_4Cl now volatilizes and dissociates in NH_3 and HCl. Since NH_3 is the lighter gas, it diffuses more rapidly through the asbestos plug than the HCl, consequently on one side of the plug we shall have an excess of HCl and on the other an excess of NH_3. The presence of these two products may be shown by passing a current of dry air through the parts of the tube on each side of the plug and then over moistened litmus paper, which will show the nature of the gases present.*

Since the density of the substance, in case of a dissociation, decreases to an extent dependent upon the temperature it is an important thing to be able to find the degree of the dissociation at any one temperature, i.e., to determine the extent of the reaction (p. 22) forming the products on the right.

This can be found from the relation of the vapor density to the dissociation, i.e., the dependence of both upon the number of moles. If, for example, α is the percentage of the gas dissociated, i.e., *the degree of dissociation*, and we start with 1 mole of the gas, then $1-\alpha$ is the undissociated portion. If there are i moles of the products formed from 1 mole of the gas, the total number of moles present at any time is

$$(1-\alpha)+i\alpha=1+(i-1)\alpha.$$

The ratio, then, of 1 to $1+(i-1)\alpha$ will be the same as that of the vapor density as it is, to the vapor density as it should be, i.e.,

$$1:1+(i-1)\alpha::d_d:d_u.$$

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*This dissociation is found by Baker (Trans. Chem. Soc. 65, 611, 1894, and 73, 422, 1898) to take place only when moisture is present. See also Abegg and Johnson, Zeit. f. phys. Chem. 61, 455–463, 1908.

Where d_u is the vapor density as it should be (i.e., as it is without dissociation), and d_d is what it actually is, for it is clear that

$$1:1+(i-1)\alpha::V_u:V_d$$

and

$$V_u:V\ ::d_d:d_u.$$

The degree of dissociation, then, is

$$\alpha=\frac{d_u-d_d}{(i-1)d_d}.$$

If a substance dissociates completely into two products, its vapor density is 1/2 what it should be; if into three, 1/3, etc.

Thus the density of NH_4Cl at a certain temperature is found to be nearly 1/2 what it should be; hence

$$NH_4Cl=NH_3+HCl.$$

And the density of $NH_2CO_2NH_4$ at the proper temperature is found to be nearly 1/3; hence

$$NH_2CO_2NH_4=CO_2+2NH_3.$$

Since when 1 mole of gas is formed from a solid or liquid against any pressure the external work done at T is, by definition, RT, when $(1-\alpha+i\alpha)$ moles are given off the work is $(1-\alpha+i\alpha)RT$.

The process of dissociation is a very common one, and proofs of it, quite as good as the one by Pebal and Than already mentioned, are numerous. A few of them are given briefly below.

PCl_5 when heated shows a green color which increases with the temperature. This is due to the dissociation into PCl_3 and Cl_2.

N_2O_4 by heat becomes brownish red, due to the formation of $2NO_2$. At 500° C. this color disappears entirely, for then $2NO_2$ breaks down into $2NO$ and O_2, both of which are colorless.

When a gas composed of a heavy metallic and a light gaseous element is dissociated by heat in an open tube, and cooled suddenly, the heavy element will crystallize out. This is due to the fact that the two gases go through the tube with a different velocity and the sudden cooling forms a compound only of what is left, the heavy element, being in excess, remaining to a certain extent in the free state. An example of this is given by Marsh's test.

The specific heat of a dissociating gas is very large owing to the fact that the heat supplied increases the dissociation as well as the temperature. When the dissociation is complete, however, the specific heat becomes constant. Thus we have for acetic acid gas:

t	129°	160°	200°	240°	280°
Sp. h't	1.50	1.27	0.95	0.64	0.480

The specific heat of a dissociating gas also varies greatly with the pressure, as does the dissociation.

The conduction of heat by a dissociating gas is very much larger than by a gas not capable of dissociating. The heat absorbed on the one side causing dissociation, and the products of dissociation diffusing to the colder portion, where they unite, giving up heat and causing a further dissociation, etc. This process continues until the gas is all dissociated, when its conduction of heat becomes normal.

Experiment shows that *a dissociation takes place to a smaller extent when the pressure is increased. This depressing effect on the dissociation is also observed when one of the products of the dissociation is already present from an exterior source.* Thus PCl_5 is almost entirely undissociated in presence of an excess of either chlorine or PCl_3, i.e., its vapor density under such conditions is found to be 104.5 in place of the calculated value 104.

Later, under Chemical Change, we shall find a formula giving the relations between the original and final substances in a chemical reaction for a constant temperature, and another showing the effect of a change in temperature, *for an increase in temperature always causes an increase in the dissociation;* but here it is simply necessary to note that dissociation depends upon temperature, pressure and presence of the products of the dissociation. The following tables will serve to show how great the effect of temperature and pressure is upon the dissociation of a gaseous substance:

Dissociation of Nitrogen Tetroxide, N_2O_4.

Atmospheric pressure.

(Density of $N_2O_4 = 3.18$; of $NO_2 + NO_2 = 1.59$; air $= 1$.)

Temp.	Sp. Gr. of Gas.	Percentage Dissociation.
26°.7	2.65	19.96
35°.4	2.53	25.65
39°.8	2.46	29.23
49°.6	2.27	40.04
60°.2	2.08	52.84
70°.0	1.92	65.57
80°.6	1.80	76.61
90°.0	1.72	84.83
100°.1	1.68	89.23
111°.3	1.65	92.67
121°.5	1.62	96.23
135°.0	1.60	98.69
154°.0	1.58	100.00

Dissociation of PCl_5.

Atmospheric pressure.

(Density $PCl_5 = 7.2$; $PCl_3 + Cl_2 = 3.6$; air $= 1$.)

Temp.	Density.	Percentage Dissociation.
182°	5.08	41.7
190°	4.99	44.3
200°	4.85	48.5
230°	4.30	67.4
250°	4.00	80.0
274°	3.84	87.5
288°	3.67	96.2
300°	3.65	97.3

Dissociation of H_2O vapor and CO_2.

Atmospheric pressure.

Absol. temp. *T*.	H_2O **Percentage dissociation,**	CO_2 **Percentage dissociation.**
1000	0.311×10^{-4}	0.212×10^{-4}
1200	0.891×10^{-3}	0.935×10^{-3}
1400	0.846×10^{-2}	0.138×10^{-1}
1600	0.049	0.102
1800	0.190	0.474
2000	0.561	1.59
2200	1.27	4.17
2400	2.73	9.00
2600	....	16.8

Dissociation of N_2O_4.

(Equal Temperatures, Varying Pressures.)

Temp.	Pressure.	Density (air = 1).	Percentage Dissociation.
18°.0	279 mm.	2.71	17.3
18°.5	136 "	2.45	29.8
20°.0	301 "	2.70	17.8
20°.8	153.5 "	2.46	29.3

The molecular weights (see definition, pp. 9 and 11) of some of the elements in the gaseous state are given below and will serve to show the importance of the process of dissociation, and how dependent the molecular weight is upon the temperature.

Arsenic.

t° C.	*M.*	
644	309	$As_4 = 300$
670	308	$As_2 = 150$
1715	157	
1736	160	

PHOSPHORUS.

313	128	
500	126.1	$P_4 = 124$
1484	105	$P_2 = 62$
1678	93.3	
1708	91	

IODINE.

253	285
1330	162

We see from these that the higher the temperature the lower is the molecular weight. Iodine at high temperatures is monatomic, as are mercury between 446°–1731°, cadmium at 1040°, tin at 1400°, and sodium and potassium. And sulphur in the gaseous state, according to the temperature, may be S_8, S_4, or S_2, the latter being the condition at 800° and above. Mixtures of these three forms can also exist, at the lower temperatures, the molecular weight of these lying between the two extremes, S_8 and S_2; at higher temperatures, 1900–2000° C., the S_2 is observed to break down further, to the extent of 50%, into the form of $2S$ (Nernst), although Biltz and Meyer found the formula weight to be 63.5 at 1719° C.

Among compounds we find the chlorides of iron and aluminium, Fe_2Cl_6 and Al_2Cl_6 only to exist at comparatively low temperatures, being present in the forms $FeCl_3$ and $AlCl_3$ at higher ones.

9. Volume, pressure and concentration.—For the complete description of a gaseous system composed either of a single gas or a mixture of gases it is essential that we have a convenient method of representing the amount of gas present. Thus far, for this purpose, we have used either the density of the gas or the volume (V) which contains 1 mole, but these are not the only forms possible, nor are they always the most convenient. The other two forms possible are *concentration*, i.e., *the number of moles per liter* (c) *and partial pressure* (p), i.e., *the pressure that would be exerted at the temperature in question if the constituent gas occupied alone the volume of the system.*

The relationship existing between V, p, and c is shown by the following, almost self-evident equations:

$$p = 22.4 \times \frac{T}{273} c \text{ atmos.,}$$

$$c = \frac{273p}{22.4T} = \frac{1}{V},$$

i.e., the pressure of 1 mole per liter at 0° (since in 22.4 liters it is 1 atmosphere) is 22.4 atmospheres, and at $T°$ is $\frac{T}{273}$ 22.4, while V, the volume of 1 mole, is the reciprocal of concentration, the number of moles per liter.

In a mixture of two gases if the total pressure of the $N(=n_1+n_2)$ moles is P the partial pressure of the individual gases will be

$$p_1 = \frac{n_1}{N} P; \quad p_2 = \frac{n_2}{N} P,$$

for the total number of moles N gives the pressure P and $\frac{n_1}{N}$ must be the fraction of the total pressure due to the gas present to the extent n_1 moles, etc.

As it is quite necessary to become familiar with the use of these terms (and especially in their application to dissociation phenomena) in our later work, the following examples are given:

At 190° C. the reaction $PCl_5 \rightleftarrows PCl_3 + Cl_2$ goes to the right to such an extent that 44.3% of the original quantity of PCl_5 is decomposed, i.e., α, the degree of dissociation, is 0.443. Since we lose 0.443 of the pentachloride and gain a like fraction of a mole of the trichloride and of chlorine, and final number of moles, starting with 1 of PCl_5, will be equal to $(1-0.443)+2\times0.443$, or 1.443.

The partial pressures may now be calculated, by taking advantage of the proportions (p. 30),

$$p_1 : P :: n_1 : N,$$

where N represents the total moles present, n_1 those of the constituent giving the partial pressure p_1, and P is the total pressure. We have, then, for the above case,

$$p_{PCl_5} = \frac{1-0.443}{1.443} \times P,$$

$$p_{PCl_3} = p_{Cl_2} = \frac{0.443}{1.443} \times P,$$

where P is the final pressure; 1 atmosphere, in case the volume increases to $1.443 \times 22.4 \frac{273+190}{100}$, and 1.443 atmospheres if it remains constant at $22.4 \frac{273+190}{273}$ liters.

To express the quantity of these three substances in terms of concentration (i.e., in moles per liter) it is only necessary to divide the final number of moles of each substance *by the total volume* of the system. Thus of the mole of PCl_5 with which we started we have but $1-0.443$ mole at equilibrium, and gain 0.443 mole of each of the two constituents. Since the final volume is $1.443 \times 22.4\,\frac{273+190}{273}$ liters, the final concentrations are

$$\frac{1-0.443}{1.443 \times 22.4\,\frac{273+190}{273}} = c_{PCl_5};$$

$$\frac{0.443}{1.443 \times 22.4\,\frac{273+190}{273}} = c_{PCl_3} = c_{\text{chlorine}}.$$

Here, naturally, the volume changes. In case the volume remains constant it is to be treated in the same way, for it is still the final volume. In the above case it would be $22.4\,\frac{273+190}{273}$.

Example.—10 gr. of PCl_5 at atmospheric pressure (in a cylinder, for instance, which is provided with a movable piston) are heated to 250° C., at which temperature α is equal to 0.8. Find the partial pressure and concentration of each of the three gases present at equilibrium.

If the PCl_5 were undissociated at this temperature the 10 gr. would occupy $\frac{10}{208.3}\,22.4\,\frac{273+250}{273}$ liters, 208.3 being the molecular, molar, or formula weight of the PCl_5. Since $\alpha=0.8$, at equilibrium we must have $1.8\,\frac{10}{208.3}$ moles of the mixture of gases (i.e., $((1-\alpha)+2\alpha)n$, where n is the number of moles present), in the final volume $1.8\left(\frac{10}{208.3}22.4\frac{273+250}{273}\right)$ liters, the total pressure remaining constant. The partial pressures, then, are $p_{PCl_5}=\frac{1-0.8}{1.8}$, $p_{PCl_3}=\frac{0.8}{1.8}$ and $p_{chlorine}=\frac{0.8}{1.8}$ atmospheres. As there are $(1-0.8)\frac{10}{208.3}$ moles of PCl_5, $0.8\frac{10}{208.3}$ moles of PCl_3, and $0.8\frac{10}{208.3}$ moles of chlorine the final concentrations (moles per liter) are $\dfrac{(1-0.8)\frac{10}{208.3}}{1.8\left(\frac{10}{208.3}22.4\frac{273+250}{273}\right)}$ for PCl_5, and $\dfrac{0.8\frac{10}{208.3}}{1.8\left(\frac{10}{208.3}22.4\frac{273+250}{273}\right)}$ each for PCl_3 and chlorine.

Since in this case 2 moles are formed from each original mole decomposed, the volume of the substance on the right is greater than the volume of that on the left, and the reaction must go backward (i.e., toward the left), when the external pressure is increased. This law is general, and is expressed by Le Chatelier as follows: "*Any change in the factors of equilibrium from the exterior causes the system to react in the direction favored by the change.*" In other words, pressure in the above case favors the formation of the substance with the smaller volume. (That a dissociating system is an equilibrium is shown by the fact that the direction of the reaction is dependent upon the direction of the temperature-change). Such a reaction as $2HI = H_2 + I_2$, on the other hand, where the same number of moles exist on either side (i.e., a reaction unaccompanied by any volume-change) should be uninfluenced by a change in pressure, as indeed is observed by experiment.

10. Variation from the gas laws. The equation of Van der Waals.—The gas laws are simply limiting laws, and while they hold in general for pressures up to 2 atmospheres, above this value differences are observed. In the case of hydrogen the product pv is always higher than it should be. This was discovered by Natterer and ascribed by Budde to the fact that the hypothetical molecules themselves occupy some of the volume. If this correction for the volume is b, then, instead of (1), we have

$$p(V-b)=RT,$$

where b is a constant for each gas.

From the formula

$$b=-\frac{RT}{p}+V$$

Budde calculated the value of b and found it to be equal to 0.00082, at which point it remained constant, for pressures varying from 1000 to 2800 meters of mercury.

In the case of hydrogen this volume-correction is satisfactory; for other gases, however, the variation is somewhat different. In general for these the compressibility at low pressure is much greater than is accounted for by the Boyle-Mariotte law, reaches a minimum and then increases so that the product pV passes through the value given by the law. This shows that there is some factor in the behavior of these gases which is absent or negligibly small in the case of hydrogen. Van der Waals ascribed this to the mutual attraction of the hypothetical molecules, which acts in the same direction as the pressure, making that larger than it seems to be. If p is the pressure and a the specific attraction, then

$$\left(p+\frac{a}{V^2}\right)(V-b)=RT,$$

which is the *equation of Van der Waals.* Here a is the so-called molecular attraction when 1 mole occupies the volume of 1 cc., and b is the volume occupied by the hypothetical molecules themselves. p and a are expressed most conveniently in terms based on $p_0=1$, where this is the original pressure in atmospheres when the gas is confined in the volume V_0. V and b are then expressed in terms of V_0.

This law, although deduced by aid of hypothetical assumptions, will hold even in the face of evidence showing these assumptions to be false. For the terms b and a are determined by experiment (b and $\frac{a}{V^2}$ expressing the discrepancy between the observed facts and the conclusions from the simple gas laws); and the worst that can befall them is a loss of name.

By this law we can understand just how gases vary from Boyle's law. For small pressure and large volume the term $\frac{a}{V^2}$ and b disappear in contrast to p and V, and the gas follows the simple law. The effect of the value of a and b upon the product pV is shown below in the form

$$pV = RT - \frac{a}{V} + \frac{ab}{V^2} + bp$$

or, for constant temperature,

$$pV = c - \frac{a}{V} + \frac{ab}{V^2} + bp.$$

When V is large and p is small $\frac{ab}{V^2}$ and bp disappear as compared with $\frac{a}{V}$; when $\frac{a}{V} = \left(\frac{ab}{V^2} + bp\right)$ we have the minimum of the variation of pV and Boyle's law holds.

These constants have been determined for the different gases from the curves for pV, and a few of the values found are given below:

a

$CO_2 = 0.00874$
$SO_2 = 0.039$
Air $= 0.037$
$H = 0.0000$

b

Air = 0.0026

CO_2 = 0.0023

H = 0.0067

The extent of the variation in the value of pV at constant temperature is shown in Figure 1. If pV is constant, the curve would be a straight line parallel to the p-axis (pV being the axis of ordinates). The higher the temperature, the more the gas behaves like hydrogen, The effect of the term $\frac{a}{V^2}$ is shown by the difference between the curve for N and for H.

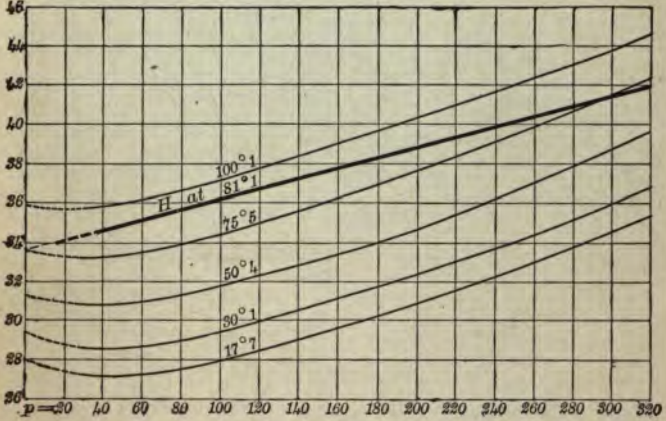

FIG. 1.—NITROGEN.

This difference can perhaps be shown in a more striking way by a comparison of the numerical values of pV. The following table is for N at 22°, the values having been found by Amagat. p is given in atmospheres.

p	pV	p	pV
1.	1.0000	109.17	0.9940
27.29	0.9894	126.90	1.0015
62.03	0.9858	251.13	1.0815
80.58	0.9875	430.77	1.2966

We see by this that up to about 12 atmospheres pV decreases in value, then follows Boyle's law, and then varies just like hydrogen. When a and b have been once determined for any pressure they may be used for all pressures. For ethylene at 20° by Van der Waals' equation, we have

p	pV	
	Obs.	Calc.
31.58	914	895
84.16	399	392
110.47	454	456
282.21	941	940
398.71	1248	1254

where p is in atmospheres, pV is multiplied by 1000, $a = 0.00786$, and $b = 0.0024$.

11. Specific heat. The first principle of thermodynamics.—When heat energy is applied to a body the temperature rises. The ratio of the amount of heat supplied to the consequent rise in temperature is called the *capacity of the body for heat*, i.e., $\frac{\Delta Q}{\Delta t}$. The value of this term depends naturally upon the original temperature of the body, its pressure, etc.

The specific heat of any substance is the capacity for heat of the unit of mass, i.e.,

$$c = \frac{1}{m} \cdot \frac{\Delta Q}{\Delta t}.$$

It has been observed that the specific heat of a gas depends upon the conditions under which it is determined. If the gas is allowed to expand under its previous pressure the specific heat, c_p, is different from that obtained when the pressure varies and the volume remains constant, c_v. Before considering the reasons for this, and finding the relation between the two values, it will be necessary for us to inquire into the nature of heat energy and its possible transformations.

Mayer in 1841 was the first to develop the subject of the theory of heat and its transformations, or Thermodynamics, as we know it to-day. Before that date heat was considered as an actual substance, which could be made to enter or leave a body. Mayer first recognized it as an energy, which could be obtained from any other energy or turned into the latter; his principal work was to determine the equivalent of heat energy, i.e., a factor by which heat energy can be given in units of mechanical energy. He was led to this conclusion by the point already mentioned, that the specific heat of gas for constant pressure is always larger than the specific heat of the same for constant volume. His reasoning was as follows: Since the specific heat at constant pressure is always greater than that for constant volume, there must be some condition in the former state which absorbs this extra heat. In the case of constant pressure the volume increases, and work must be done to overcome the atmospheric pressure, which would keep the volume constant. It is a logical consequence, then, to consider that this extra heat is simply the amount necessary to do the mechanical work of expansion. In other words, a certain number of calories are found to be equal to a definite number of mechanical units; this value for one calorie is the *mechanical equivalent of heat.* This term may be calculated as follows: The difference between the heats necessary to raise the temperature of 1 gram of air 1° C. under the two conditions is by experiment

$$c_p - c_v = 0.0692 \text{ cal.}$$

This 0.0692 cal. is the heat which is equivalent to the work necessary to expand 1 gram of air 1/273 of its volume at 0°. Imagine 1 gram of air at 0° enclosed in a tube with a cross-section of 1 square centimeter. It will occupy the space of 773.3 cms., if the pressure is 76 cms. of Hg, for 1 gram of air occupies under these conditions 773.3 cc., which is the specific volume of air. An increase of temperature of 1° C. will expand this volume 1/273, i.e., 2.83 cms. The weight of the atmosphere, 1033 grams, will then be raised through this distance. The work necessary to do this is

$$1033 \times 2.83 = 2923.4 \text{ gr.-cms.},$$

which is equivalent to 0.0692 calorie. For one calorie, then, we have

$$\frac{2923.4}{0.0692} = 42245 \text{ gr.-cms.},$$

which is the *mechanical equivalent of heat.*

Joule transformed a known amount of mechanical work into heat by friction, and found from the heat developed that

$$1 \text{ cal.} = 42355 \text{ gr.-cms.}^{*}$$

The great consequence of Mayer's work is what is known as the first principle of thermodynamics. According to this *the energy of any isolated system is constant,* i.e., when energy seems to disappear it is simply transformed into another form. If, for example, a gaseous body is heated, its internal energy is increased; if the

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* A liter-atmosphere is the work necessary to force the weight of the atmosphere upon a square decimeter through a decimeter. We have then

$$1 \text{ L. A.} = \frac{1033 \times 10 \times 100}{42600} = 24.25 \text{ cals.},$$

42600 being the mechanical equivalent now used, the average of a number of late determinations.

R, the molecular gas constant, which is equal to 84800 gr.-cms., or 0.0821 L. A., is equal practically to 2 cals.

If the reader cannot follow the mathematics involved in the derivation of the final formulas, he can simply turn to their physical meaning, which is given below them in italics, and will thus be able to use the important relations, even though he cannot derive them.

volume increases, however, a certain amount of this heat is used to overcome the atmospheric pressure, and the increase of the internal energy is less than would otherwise be the case. If U is the internal energy and the amount of heat dQ is supplied to the body, then

$$dQ = dU + dW, \tag{2}$$

where dW is the amount of work done by the body by virtue of the heat absorbed, and dU is the corresponding increase in the internal energy. If we consider the work as overcoming a resistance it is more readily handled. Suppose the gas to increase its volume, the pressure remaining constant; then for 1 mole

$$dW = pdV,$$

where p is the intensity factor and V the capacity factor of volume energy. Substituting this value of dW in the former equation (2), we have

$$dQ = dU + pdV, \tag{3}$$

where dU, dQ, and pdV are expressed in absolute units. If dU and pdV are given in mechanical units, then (3) becomes

$$dQ = \frac{dU + pdV}{A}, \tag{4}$$

where A is the mechanical equivalent of heat, i.e., the value of 1 calorie. We shall use the form (3), however, always remembering that dQ, dU, and pdV are expressed in the same units. The internal energy U of a gas may be considered as a function of pressure and volume, of pressure and temperature, or of volume and temperature. Of these we shall only consider the case where temperature and volume are variable. We have then

$$dU=\frac{dU}{dT}dT+\frac{dU}{dV}dV.$$

The term $\frac{dU}{dV}dV$, however, is equal to zero, for the internal energy of a gas, according to Gay-Lussac's experiment, remains the same after a change in volume provided no external work is done. By this experiment it was shown that the expansion of a gas into a vacuum does not change the temperature of the system; although there is a slight increase in the temperature of the exhausted vessel and a slight decrease in the other, they compensate one another. Equation (3) becomes then

$$dQ=\frac{dU}{dT}dT+pdV.$$

If V is constant, i.e., $dV=0$, then

$$dQ=\frac{dU}{dT}dT.$$

This term, $\frac{dU}{dT}$, the increase in the internal energy caused by an increase of temperature, is, however, the molecular specific heat for constant volume; hence

$$dQ=\frac{dU}{dT}dT=C_v dT \text{ (for constant volume).}$$

If the pressure remains constant and the volume varies, i.e., if dV does not equal zero, then pdV does not disappear, and we have

$$(5) \qquad dQ=C_v dT+pdV,$$

or

$$\frac{dQ}{dT}=C_v+\frac{pdV}{dT}.$$

This term, $\frac{dQ}{dT}$, under these conditions is the specific heat at constant pressure, i.e.,

$$(6) \qquad C_p=\frac{dQ}{dT}=C_v+\frac{pdV}{dT}.$$

By differentiating (1), p remaining constant, we have

$$pdV=RdT,$$

Substituting this in (6), we find

$$C_p = C_v + R, \tag{7}$$

when C_p and C_v refer to the specific heats for 1 mole of gas, and R is the molecular gas constant.

If in the system no heat is absorbed or given up by conduction or radiation, i.e., $dQ=0$, we have *an adiabatic process.* From (1), by complete differentiation, we have

$$pdV + Vdp = RdT.$$

If in (5) we eliminate dT, by this equation, remembering that

$$C_v + R = C_p,$$

we obtain

$$dQ = \frac{C_v}{R} Vdp + \frac{C_p}{R} pdV. \tag{8}$$

Since in an adiabatic process $dQ=0$,

$$0 = \frac{C_v}{R} Vdp + \frac{C_p}{R} pdV.$$

And, representing the ratio of the specific heats, $\frac{C_p}{C_v}$, by k (for air = 1.41), we have

$$Vdp + kpdV = 0,$$

or

$$k\frac{dV}{V}+\frac{dp}{p}=0.$$

And by integrating between the limits p, V, and p_1, V_1, we have

$$\log_e p+k \log_e V=\log_e p_1+k \log_e V_1,$$

i.e.,

$$k=\frac{\log_e p_1-\log_e p}{V-V_1}, \tag{10}$$

or, in another form,

$$\frac{p}{p_1}=\left(\frac{V_1}{V}\right)^k.* \tag{11}$$

From (11) we see that for an adiabatic process the volume changes less for a change in pressure, or the pressure changes more for a change in volume, than is the case when the temperature remains constant (i.e., an isothermal process). *For rapid compressions or expansions of a gas, then, we have the relation,*

$$p_1:p::V^k:V_1{}^k,$$

where $k=\frac{c_p}{c_v}$, *the ratio of specific heat at constant pressure to that at constant volume, in place of*

$$p_1:p::V:V_1,$$

which is true when the process is very slow and the temperature remains constant.

$$*\left(\frac{V_1}{V}\right)=\left(\frac{v_1}{v}\right).$$

Boyle's law holds also of course for an adiabatic change *after* the temperature produced by the change of volume has been reduced to the original one.

In equation (11) we know that

$$pV=RT$$

and

$$p_1V_1=RT_1;$$

hence

$$\frac{pV}{p_1V_1}=\frac{T}{T_1}.$$

But, by (11)

$$\frac{V}{V_1}=\left(\frac{p_1}{p}\right)^{\frac{1}{k}}.$$

Whence, by substitution,

$$\frac{T}{T_1}=\left(\frac{p}{p_1}\right)^{\frac{k-1}{k}}. \tag{12}$$

By substituting the value of $\frac{V}{V_1}$ instead of that of $\frac{p}{p_1}$, we obtain

$$\frac{T}{T_1}=\left(\frac{V_1}{V}\right)^{k-1}. \tag{13}$$

The temperatures to be obtained by the expansion of a gas at the temperature T can be found from(12). Examples of this are given in Table I.

TABLE I.*

TEMPERATURES CAUSED BY ADIABATIC EXPANSION OF AIR. $k=1.4$.

p (atmospheres).	t (initial from T).	t' (final from T_1).
100	$71°.5$	$-201°.5$
200	$58°.5$	$-213°.5$
300	$52°.0$	$-221°.0$
400	$47°.9$	$-225°.0$
500	$44°.8$	$-228°.2$

The temperatures are those of the air as it expands. Owing to the specific heat of the vessels used, it is impossible to reach these temperatures in anything in contact with the gas, although very low temperatures may be thus obtained.

The idea involved in equation (7), i.e.,

$$M(c_p - c) = R,$$

is also very valuable, for it shows that for all gases the difference between the molecular specific heats is $R=2$ cals. This equation can also be derived in the following simple way. The difference between the molecular heat at constant pressure and that at constant volume is obviously equal to the heat equivalent of the work of expansion, for the constant pressure condition involves external work while the constant volume condition is a no-external-work condition. By definition however, the external work done in the formation of a mole of gas from negligible volume, against any pressure, at the temperature T is RT. At the temperature $T+1$, i.e., after heating the gas 1°, the external work would be $R(T+1)$; hence the work done by the expansion of 1 mole of gas on the heating of 1°, is equal to

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* For other calculations involving the above formulas see Falk, Jour. Am. Chem. Soc., 28, 1517, 1906, and 29, 1536, 1907.

$$R(T+1)-RT=R,$$

and

$$M(c_p-c)=R=2 \text{ cals.}$$

Naturally the terms Mc and Mc_v are to be determined at the same temperature. That this relation holds is shown by the following list of experimentally determined values (Clausius-Ostwald).

MOLECULAR SPECIFIC HEATS.

Name.	Const. Pres.	Const. Vol.	Ratio (k).
Oxygen	6.96	4.96	1.40
Nitrogen	6.93	4.83	1.41
Hydrogen	6.82	4.82	1.41
Chlorine	8.58	6.58	1.30
Bromine	8.88	6.88	1.29
Nitric oxide (NO)	6.95	4.95	1.40
Carbon monoxide	6.86	4.86	1.41
Hydrochloric acid	6.68	4.68	1.43
Carbon dioxide	9.55	7.55	1.26
Nitrous oxide (N_2O)	9.94	7.95	1.25
Water	8.65	6.65	1.28
Sulphur dioxide	9.88	7.88	1.25
Ozone	—	—	1.29

This relation gives us another (pp. 9, 11) definition of molecular or formula weight in the gaseous state. *The* *molecular or formula weight of a gas is that number which when multiplied by the difference between the specific heat at constant pressure and that at constant volume gives a value of 2 cals.*

The ratio $k\left(=\frac{c_p}{c_v}\right)$ of equation (11) is also employed to find the number of combining weights contained in a formula weight of a gas. This is purely an empirical relation, it having been observed that known monotomic gases, mercury for example, give $k=1.667$, diatomic ones about 1.4, etc.; the greater the number of atomic weights to the formula weight, the smaller the value of the relation $\frac{c}{c_v}$. An example of this application is given by Ramsay in the work on argon, where the combining weight, owing to the non-existence of any compounds with this, is unknown.

By combining the equation

$$M(c_p-c_v)=2$$

with the value of the relation $\frac{c_p}{c_v}$ for the gas in question, it is apparent that, so long as the gas laws hold, the value of Mc_p (or of Mc_v) is the same for all so-called monatomic gases. Naturally Mc_p (or Mc_v) will have a different value for a diatomic gas, but that value will remain constant, under the above condition, for all diatomic gases; and the same is true when for all triatomic, etc., gases. In this way it is possible to get an approximate value of c_p or c_v for any gas simply from the knowledge of the constant value, Mc_p (or Mc_v) for that type of gas, and the molecular weight of the gas.

12 **Determination of the specific heat of gases.**—The specific heat for constant volume c_v cannot be determined directly with accuracy, since the vessel containing the gas absorbs so much more heat than the gas itself. Even under the most favorable conditions the ratio of the absorption of heat by the gas to that by the vessel is 1:55.

From the specific heat for constant pressure and the ratio $k=\frac{c_p}{c_v}$, c_v can, however, be found indirectly.

The specific heat at constant pressure is determined by passing a certain volume of the gas, heated under constant pressure, to a certain temperature, through the worm of a calorimeter and observing the consequent increase in the temperature of the water. We know then the number of calories which causes a certain temperature to exist in the known volume of the gas; and from this data it is easy to calculate the specific heat, c_p. The value of the molecular specific heat for constant pressure for all gases seems to converge toward the value

6.5 at the absolute zero. We have in general the relation

$$Mc_p = 6.5 + aT,$$

where a is a constant for each gas and is the larger the more complex the formula. For a we find the following values: for H_2, N_2, O_2, and CO, $a = 0.001$, $NH_3 = 0.0071$, $CO_2 = 0.0084$, $C_6H_6 = 0.0510$, ether = 0.0738, $H_2O = 0.0089$, $C_2H_4 = 0.0137$, $CHCl_3 = 0.0305$, $C_2H_5Br = 0.0324$, $CH_3COOC_2H_5 = 0.0674$, $C_3H_6O = 0.0403$, $N_2O = 0.0089$. This formula may be used in the following way to find the value c_p. For C_6H_6, $a = 0.0510$; hence at 50°, we have

$$c_p = \frac{6.5 + 0.0510 \times 323}{78} = 0.295,$$

while Wiedemann found 0.299 experimentally.

The ratio $k = \frac{c_p}{c_v}$ can be found easily by the method of Clément and Desormes, even though the individual values of c_p and c_v are unknown.

A glass balloon, holding about 20 liters, is provided with a brass stop-cock and a manometer. From this vessel the air is partially rarefied and the pressure observed by aid of the manometer. Let this initial pressure be p_0 and the atmospheric pressure be P. If the cock is now opened for half a second air will rush in until the external and internal pressures are the same. As the air goes in, however, heat will be developed, which, as it is not removed, will increase the temperature of the gas according to the law of adiabatic compression (p. 46). By the process we have increased the pressure from p_0 to P. If the initial specific volume is v_0 and the final one is v, then k can be determined from the equation

$$\frac{P}{p_0}=\left(\frac{v_0}{v}\right)^k.$$

The final specific volume is not known yet, however. To find this we wait until the flask and air have been reduced to the temperature of the surrounding air and again measure the pressure. If this pressure is p at the temperature t, then

$$v_0:v::p:p_0,$$

or

$$\frac{P}{p_0}=\left(\frac{p}{p_0}\right)^k.$$

and

$$k=\frac{\log P-\log p_0}{\log p-\log p_0}.$$

In one experiment with air $P=1.0036$, $p_0=0.9953$, and $p=1.0088$ atmospheres; hence

$$k=1.3524.$$

13. The second principle of thermodynamics.—By the first principle we have found that a certain amount of heat is equivalent to a certain amount of work. If we consider, however, the possible means of transforming heat into work we find that a certain condition must be fulfilled, i.e., the heat must go from a warmer to a colder body. In other words, heat can only produce work by going from a higher to a lower temperature. This condition has been expressed in other words. For example, *heat of itself can never go from a colder to a warmer body without work being used upon it. A perpetual motion of the second kind is impossible.*

A device to produce a perpetual motion of the second kind would be a machine which would run, for example, from the heat of the sea. It is related to the second just as an ordinary perpetual motion is related to the first principle.

Since heat can only be transformed into work by a transference of heat from a higher to a lower temperature, it is important to know the relation which exists between the amount of heat transferred as heat and that transformed into work.

For this investigation it is necessary that all the work done be external work, which can be readily observed, and then compared with the known amount of heat. We employ for this purpose a process which was originated in 1824 by Sadi Carnot and which is known as the Carnot cycle. The arrangement is such that the final state is identical with the initial one, i.e., before and after the operation the body contains exactly the same amount of energy. Then the relation between the heat transferred and the work done is very readily obtained. Naturally no heat must be lost by radiation or conduction, or the final result will be incorrect; for this reason the process is an ideal one and cannot be realized practically. Since all transference of heat and work is assumed to take place without differences in temperature and pressure the process may go in either direction, i.e., it is reversible. This condition of reversibility is never obtained in practice, so that the relation which we find is the limit under the most favorable conditions.

14. **The thermodynamic cycle.***—A gas, on absorbing heat, expands and does work until its temperature, which must have been higher than that of the environment, falls to this. By this process heat at a high temperature is absorbed by the gas and partly transformed into external work. When the temperature of the gas is reduced to that of the environment no more work can be done. The object of this process we are to assume as carried out is to find the relation of heat absorbed to the heat which is transformed into work under ideal conditions.

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* If the reader does not follow the mathematical derivation, he may simply turn to the physical meaning of the relation derived so that he can at least make use of it.

1. Assume an ideal gas enclosed in a cylinder with a movable piston at a certain temperature and pressure. The cylinder is now placed in a heating-bath at the temperature T_1, and the volume is allowed to increase under a constant pressure which is just greater than that of the atmosphere. By this expansion the gas will cool. Here, however, we assume heat to be absorbed by it to such an extent that the temperature remains constant. If the heat absorbed by the gas is Q_1, its initial volume v_1, and its final one v_2, and the constant temperature T_1, then the work done by the gas will be equal to $\int_{v_1}^{v_2} p dv$. Since the temperature remains constant, equation (5) becomes

$$dQ_1 = 0 + pdv;$$

or, since $p = \frac{rT}{v}$,

$$dQ_1 = rT\frac{dv}{v}$$

or

$$Q_1 = rT_1 \log_e \frac{v_2}{v_1}. \tag{14}$$

2. The gas is next allowed to expand adiabatically until the temperature falls to T_2. For this, the new volume being v_3, we have the relation

$$\frac{T_1}{T_2} = \left(\frac{v_3}{v_2}\right)^{k-1}. \tag{15}$$

3. Next the pressure is increased until the volume decreases to v_4, heat being removed to the amount Q_2, so that the temperature remains constant at T_2. The work done here by the gas is $-\int_{v_3}^{v_4} p\,dv$; we have then

$$Q_2 = rT_2 \log_e \frac{v_3}{v_4}. \tag{16}$$

4. Finally, the gas is compressed adiabatically until the original volume v_1 and the original temperature T_1 are reached. This can be arranged by choosing v_4 of the proper size. We have for this relation

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_4}\right)^{k-1}. \tag{17}$$

We have thus carried the gas through a series of changes, and have finally the same state as that from which we started. The amount of heat Q_1 is absorbed at the higher temperature T_1, and a smaller amount Q_2 is given up at the lower temperature T_2, and a certain amount has been transformed into work. The amount of heat which is equivalent to the work done is equal to $Q = Q_1 - Q_2$. The heat Q_2 has simply been transferred from the emperature T_1 to T_2.

The relation between Q_1 and Q_2 is given by equations 14) and (16)

$$\frac{Q_1}{Q_2}=\frac{rT_1 \log_e \frac{v_2}{v_1}}{rT_2 \log_e \frac{v_3}{v_4}}.$$

By (15) and (17), however,

$$\frac{v_2}{v_1}=\frac{v_3}{v_4}, \quad \text{i.e.,} \quad \log_e \frac{v_2}{v_1}=\log_e \frac{v_3}{v_4};$$

hence

$$\frac{Q_1}{Q_2}=\frac{T_1}{T_2},$$

i.e., *the amounts of heat absorbed and liberated are proportional to the absolute temperatures.*

The amount of heat transformed into work is $Q=Q_1-Q_2$. We have then

$$\frac{Q_1-Q_2}{Q_2}=\frac{T_1-T_2}{T_2}$$

and

$$\frac{Q_1-Q_2}{Q_1}=\frac{T_1-T_2}{T_1}.$$

From the two equations above we may conclude that, in reversible processes, *the work done, or to be done, by the transformation of heat into work is to the amount of* *heat absorbed at the temperature* T_1 *(or liberated at* T_2*) as the temperature interval through which the heat has fallen (or must fall) is to the absolute temperature* T_1 *(or* T_2*).*

Thus at a boiler temperature of 200° and a condenser temperature of 50°, the fraction of the heat absorbed which would be transformed into work under ideal conditions is $\frac{150}{273+200}$, and the ratio of heat transformed into work to the heat evolved as heat at T_2 is, at greatest, $\frac{150}{273+50}$. *If* T_2 *were the absolute zero, then, and only then, would all heat be transformed into work;* otherwise the ratio is always less than 1. Naturally in the above both heat and work must be expressed in the same units.

Although we have derived this relation for gases it is equally true, for all systems where heat is being transformed into any kind of work.

CHAPTER III.

THE LIQUID STATE.

15. Distinction between liquids and gases.—Liquids are distinguished from gases by the fact that they possess a volume of their own, which, although dependent upon pressure and temperature, cannot be changed to any extent by them.

From the standpoint of experiment all we can say of a liquid, as compared to a gas, is that it contains less energy than the former, for energy is always absorbed by a liquid when it is being transformed into a gas. On hypothetical grounds it is said that the attraction between the molecules of a liquid is greater than between those of a gas.

Since the volume in the gaseous state is always greater than that in the liquid state, a greater temperature is necessary to cause a liquid to boil when the pressure over it is increased. And, conversely, a liquid boils more readily (i.e., at a lower temperature), when the pressure over it is decreased. (See Le Chatelier's theorem, p. 33).

16. Connection between the gaseous and liquid states.—If at constant temperature a gas is subjected to a constantly increasing pressure, its state may change in one of two ways according to the conditions:

a. This case has already been considered under gases. The volume at first changes more rapidly than the pressure, next in the same ratio, and finally more slowly. When the pressure becomes very high a further increase has but a slight effect upon the volume.

b. Here the relation between pressure and volume is quite different, although the first step is the same, i.e., the volume changes more rapidly than the pressure. The ratio here, however, in contrast to *a*, increases continually. When a certain pressure is reached a new phenomenon is observed: the gas is no longer homogeneous; one part has separated which behaves differently from the rest, i.e., the gas is partly liquefied. For a constant temperature this liquefying pressure remains constant, while the volume decreases steadily, i.e., for one pressure we have a whole series of volumes. An increase in the external pressure has no lasting effect upon the internal pressure (which still remains as it was), but it causes the volume to decrease more rapidly. Only after the whole gas has been liquefied can the pressure be increased. Then, however, we shall compress only the liquid, just as in the last stage of *a* we compressed the gas.

The condition which causes a gas under compression to follow *a* or *b* is the temperature. If this is above a certain point, which depends upon the nature of the gas, process *a* will be followed; if below this point, process *b*. This was the first recognized by Andrews in 1871. If, for example, we compress CO_2 gas, keeping the temperature at 0°, the volume changes more rapidly than the pressure, and at a pressure of 35.4 atmospheres the gas condenses to a liquid. The higher the temperature, under 30°.92, the higher the pressure must be to cause condensation; but above 30°.92 no condensation is possible. Thus:

t	*p*	*t*	*p*
31°,	impossible to liquefy it.	−21° =	21.5 atmospheres.
30°.92 =	73.6 atmospheres.	−40° =	11.0 "
30° =	73.0 "	−59°.4 =	4.6 "
13°.1 =	48.9 "	−70°.6 =	2.3 "
0° =	35.4 "	−78° =	1.2 "

Andrews called the temperature 30°.92 the *critical temperature*. Correspondingly we call the pressure which is necessary to liquefy the gas, at the critical temperature, the *critical pressure* (73.6 atmos. at 30°.9), and the volume which the gas or liquid occupies ($d_l = d_g$), under these two conditions, the *critical volume*.

The best method of showing the behavior of a gas under compression is by plotting a curve in a system of coordinates where the pressures are laid out upon the is of ordinates, and the volumes upon the axis of scissæ. In these two curves the horizontal parts, hich show constant pressure for varying volume, in-

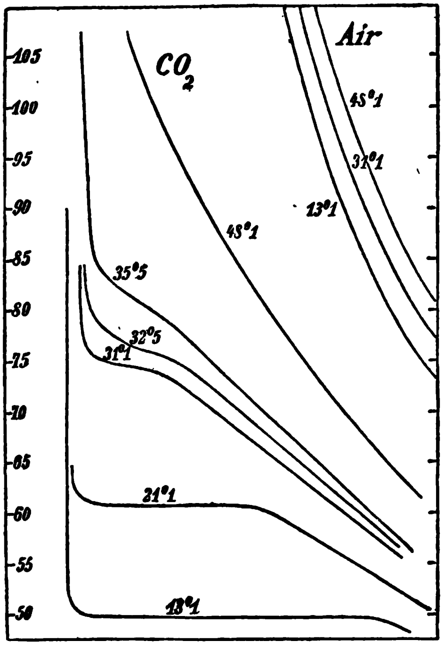

FIG. 2.

dicate that the gas liquefies. The vertical parts refer to the liquid state, while all others refer to the gaseous state.

Fig. 2 shows the behavior of CO_2 and air, the ordiates being pressures in atmospheres. At 31°.1 CO_2 ere is no horizontal part, i.e., no varying volume for constant pressure; the gas does not liquefy, since it is above its critical temperature. For all temperatures below 31°.1 the horizontal part is present, i.e., the gas liquefies under a sufficient pressure. Under all these pressures air remains a gas and behaves as CO_2 does when above 31°C.

The critical temperature of a mixture of two liquids can be calculated in general by the formula,

$$t_{\text{mixt.}} = \frac{pt_1 + (100 - p)t_2}{100},$$

where p represents the percentage by weight of the liquid 1 and, naturally, $100 - p$ that of the liquid 2. In other words, critical temperature is an *additive* property. (For further information on this subject, see Pawlewski, Ber. 15, 460 and 2460, 1882, and Schmidt, Lieb. Ann. 266, 266, 1891, and for an exception to the general rule, see Kuenen, Phil. Mag. 40, 173, 1895.)

When a solution of a solid substance is heated to its critical temperature it is observed that there is no separation of solvent and solute, and that apparently the gaseous solvent has the same power to dissolve the substance that the liquid one had.

17. Vapor-pressure and boiling-point.—The vapor-pressure of a liquid is the pressure to which, at any fixed temperature, it will evaporate in an exhausted space. If the vapor thus formed is removed, naturally more vapor will form, and by successive removals of portions in this way the entire amount of liquid may be evaporated. To cause a liquid to evaporate continuously, then, it is necessary to remove the pressure of the vapor above it. This may be done as above, or the same condition may be attained by making the exhausted space large enough to contain the vapor of all the liquid and yet not reach a high enough pressure to prevent further evaporation. This latter condition is indeed obtained in the open air when the vapor pressure of the liquid is increased to such an extent by heat that it exceeds the counter-pressure of the atmosphere. The temperature necessary for this is called the *boiling-point* of the liquid, the boiling-point designating that temperature, at atmospheric pressure, at which liquid and gas can exist together in all proportions. Every external pressure corresponds to a certain temperature, and these two magnitudes increase and decrease together. At the critical temperature the significance of vapor-pressure is naturally lost. For every pressure under the critical one, however, there is a certain temperature at which gas and liquid may exist together in all proportions: this temperature is the boiling-point at that pressure. Correspondingly, for every temperature under the critical one, there is a certain pressure at which gas and liquid may exist in equilibrium in all proportions: this is the vapor-pressure at that temperature.

Although the boiling-point of a liquid has always been supposed to offer the best criterion as to its purity, Gutmann (Trans. Chem. Soc., 87, 1037–1042, 1895, Jour. Am. Chem. Soc. 29, 345–348, 1907) has called attention to the fact that the freezing-point is a much surer indication, and proves it with results obtained with liquid air as the freezing mixture.

The vapor-pressure of a liquid may be determined in one of several ways. One method of theoretical interest which gives good results is by J. Walker. A current of dry air is passed through the liquid which is held at constant temperature and the loss in weight of the liquid observed. The air in passing through the liquid will absorb an amount of vapor proportional to the vapor-pressure of the liquid. If V is the volume of air which in passing through the liquid absorbs the weight of 1 mole, then in that volume we have the relation

$$pV=RT,$$

where p is the vapor pressure of the liquid at the temperature T, i.e., the *partial pressure* of the vapor in the air which has passed through.

If v_x is the volume of air which absorbs x grams of the liquid with the molecular weight M *in the gaseous state*, then we have

$$pv_x=\frac{x}{M}RT,$$

or

$$p=\frac{x}{Mv_x}RT.$$

The term v_x here represents the total volume containing the x grams, i.e., that of vapor and air, but that of the latter may be taken as a rule as the volume of the other is small in comparison.

If we compare two liquids at the same temperature, passing equal volumes of air through them,

$$\frac{p}{p'}=\frac{x}{M}\times\frac{M'}{x'},$$

or

$$p=\frac{x}{M}\times\frac{M'}{x'}p',$$

where M and M' are the molecular weights of the substances in *gaseous* form.

This equation may also be used, for one liquid alone, in its original form,

$$pv_x=\frac{x}{M}RT.$$

Here naturally we must assume that the saturated vapor behaves as a more permanent gas would i.e., obeys the gas laws. The only difficulty in the use of these formulas is *the necessity of having the same dimensions on either side.* If p be expressed in atmospheres, V in liters and R in liter-atmospheres little difficulty will be experienced. x and M are then found in grams, the ratio $\frac{x}{M}$ being equal to the number of moles going into the gaseous state. For further information on this valuable method, see Walker, Zeit. f. phys. Chem., 2, 602, 1888; Will and Bredig, Ber., 22, 1084, 1889; Orndorff and Carrell, Jour. Phys. Chem., 1, 753, 1897; Perman, Proc. Roy. Soc., 72, 72, 1903; Carveth and Fowler, J. Phys. Chem., 8, 313, 1904; Berkeley and Hartley, Proc. Roy. Soc., 77, 156 and 78, 68, 1096; and Lincoln and Klein, Jour. Phys. Chem., 11, 318, 1907.

18. The heat of evaporation.—For the transformation of a liquid into its gaseous form a considerable amount of heat is necessary. There are two causes for this absorption of heat. The volume must be increased against atmospheric pressure, and the liquid must be transformed into the gaseous state. The former is of the least value. Its amount, by definition, may be calculated from $pV=RT=2T$ cals. (see p. 11); i.e., for every mole of water-vapor formed from liquid water, at 100°, $2\times(273+100)=746$ cals. are used for the expansion. Since the heat of evaporation of 1 mole (18 grams) of H_2O to steam at 100° is 9650 cals., and the amount necessary for the expansion is but 746 cals., it will be observed that the difference in energy-content of the two states is very considerable.

The ratio of the molecular heat of evaporation (=molecular weight *as a gas* multiplied by the heat of evaporation of 1 gram) to the absolute boiling-point, at atmospheric pressure, has been found experimentally by

Trouton (Phil. Mag., (5), 18, 54, 1884) to be a constant for a very large number of substances, and equal to approximately 21, i.e., $\frac{Mw}{T_{b.p.}}=21$, but Nernst has found this constant to vary with the temperature and has suggested two other forms* of the equation, which give satisfactory results for a large number of liquids. Later these equations were simplified by Bingham (Jour. Am. Chem. Soc., 28, 723–731, 1906) to the form

$$\frac{Mw}{T_{b.p.}}=17+0.011T_{b.p.}$$

Although the substitution of the values of M, as a gas, w, and $T_{b.p.}$ in this equation shows that it holds for a very large number of substances, certain others give a greater value to the left side than to the right. This is interpreted as meaning that the substance as a liquid has a larger molecular weight than it has as a gas, i.e., is associated, and consequently requires an extra amount of energy, over that requisite for a simple evaporation, to perform the work of disassociation; and the difference in the values of the right and left sides is assumed to be an approximate measure of the amounts of the association. *When the substitution of the values of M, as*

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* $\frac{Mw}{T_{b.p.}}=9.5\log.T_{b.p.}-0.007T_{b.p.}$ and $\frac{Mw}{T_{b.p.}}=8.5\log T_{b.p.}$. Gött. Nach., 1906.

a gas, w, and $T_{\text{b.p.}}$ gives the same value for the two sides of the equation, then, the substances is regarded as NON-ASSOCIATED, *i.e., to have the same molecular weight in both the liquid and gaseous states; it is not possible, however, to calculate from the equation the extent of the association; when the two sides are not identical, in other words, we cannot solve for M and consider that the molecular weight as a liquid.*

It will be seen that this law is simply an extension of our "work" definition of molecular weight as a gas (p. 11); for the equation provides that not only the external work of formation of a mole of gas from negligible volume, but also the *total heat* of formation, is dependent with non-associated substances *only* upon the temperature of formation. Naturally, when the liquid must also disassociate in forming the gas, we would expect the total heat for each specific case to be smaller or larger, according as heat is absorbed or evolved by the process of disassociation, the amount of which would depend upon the nature of the substance.

Another equation which can be used for the calculation of the heat of evaporation of *non-associated* liquids is given by Mills (Jour. Phys. Chem., 9, 402; 10, 1; 11, 132; 11, 154) in the form $\frac{Mw - \text{ext. work}}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}$, where d is the density as a liquid and D as a gas. This formula can be used, contrary to the Trouton-Bingham relation, at temperatures other than the boiling-point at atmospheric pressure.

Still another equation, holding for non-associated liquids, has been derived as follows by Crompton (Proc. Chem. Soc., 17, 61, 1901): Assume that the gas laws hold rigidly for a saturated vapor, and, further, that theoretically it is possible at constant temperature, and by compression alone to reduce the volume of a mole of gas, V_g $(=Mv_g)$, to that occupied by the liquid, V_l $(=Mv_l)$,* without any change in state occurring and the gas continuing to obey the law throughout the compression. The work done in causing this change of volume will be equal, then, to

$$\int_{V_l}^{V_g} p\,dV = \int_{V_l}^{V_g} \frac{RT}{V}\,dV = RT \log_e \frac{V_g}{V_l},$$

and as no change in temperature takes place, heat equivalent to this will be given out. The gas will now occupy the volume which would be occupied by the liquid, but of itself it will not retain its volume. In order to obtain it in such a state that it will do this it is necessary to remove its ability to expand. By removing an amount of energy equal to that expended in compressing the material, viz., $RT\log_e\frac{V_g}{V_l}$, we shall, however, also remove this power of expansion. The total heat given out, then, by the production of the liquid from the vapor is $2RT\log_e\frac{V_g}{V_l}$, and this is equal to the latent heat of evaporation of the molecular amount, i.e.,

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* In this, instead of assuming the volume of the liquid as negligible (definition, p. 11), for the sake of greater accuracy, we are to consider it.

$$l=Mw=2RT\log_e\frac{V_g}{V_l},$$

or, since the ratio of the molecular volumes $\frac{V_g}{V_l}$ under normal conditions is the same as that of the specific volumes, or inversely as the specific densities, and using Brigg's logarithms, we have

$$l=Mw=2RT\log\frac{v_g}{v_l}\times\frac{1}{\cdot 4343}.$$

Thus, since for CO_2 at $T=248$, $d_l=1.10$, $d_g=0.044$, and $M=44$, we find $w=71.91$ calories, where the experimental value is 72.23.

This formula, which can also be used at any temperature, according to Mills, gives very accurate values at temperatures at which the vapor-pressure is high, but values which are too large for those temperatures giving low vapor-pressures; the divergence, at high vapor-pressures, being greater than one calorie only for a few cases (see Mills, l.c.). The term $\frac{Mw}{T_{\text{b.p.}}}$ of the law (p. 69) is equal according to this equation to $2R\ (\log_e V_g - \log_e V_l)$, which for many liquids gives values lying between 22.8 and 23.9.

The heat of evaporation, however, also varies with the temperature. The expression for this variation is derived as follows: (1) Allow 1 mole of liquid to vaporize at the boiling temperature, T, and then heat this volume, holding it constant, to the temperature $T+t$. The gas in expanding has done the work $pV=RT$ and has absorbed the heat Mc_vt in going to the higher temperature, while the latent heat of evaporation is l_T. (2) We reach the same final state by first heating the liquid to $T+t$, by which the heat Mc is absorbed, and then allow the gas to form at $T+t$. The work of expansion here is $pV=R(T+t)$, and the latent heat l_{T+t}. By these two processes we have reached the same final state from the same initial one, so by the principal of the conservation of energy the loss in energy is the same in both cases. We have then

$$RT-(l_T+Mc_vt)=RT+Rt-(l_{T+t}+Mct),$$

or

$$Mc_v+R-Mc=\frac{l_{T+t}-l_T}{t},$$

and, since by (7), see p. 48, $Mc^v+R=Mc_p$,

$$Mc_p-Mc=\frac{l_{T+t}-l_T}{t}=\frac{\Delta l}{\Delta T}, \quad \text{or} \quad c_p-c=\frac{\Delta w}{\Delta T},$$

i.e., *the latent heat of evaporation, in the neighborhood of any temperature, increases per degree by an amount equal to the specific heat of the gaseous state at constant pressure, minus the specific heat of the liquid, both at that temperature.* Since the specific heat of the gas is always less than that of the liquid, the increase is negative, i.e., the heat of evaporation always decreases with increasing temperature. c for benzene at 50° is 0.45, c_p for 50° (see p. 52) $=0.295$, hence the temperature coefficient of the heat of evaporation of benzene around 50° is -0.155 cal. per degree, for $\frac{\Delta w}{\Delta T}=0.295-0.45=-0.155$; the value -0.158 having been found by experiment, the difference being within the experimental error.

The substance must have the same molecular weight in both the gaseous and liquid state if correct results are to be obtained by this formula. If associated in liquid form, the result here will be too small, owing to the fact that Mc will be smaller than the proper value.

19. The relation between vapor-pressure, heat of evaporation, and temperature.—An equation showing the relation between these three quantities can be found as follows: Start with 1 gram of liquid at T, and under its own vapor-pressure p. Heat $\varDelta T^\circ$ and assume it to be completely transformed into gas. During this process heat equal to $w_{T+\varDelta T}$ will be absorbed at the temperature $T+\varDelta T$, the volume will change from v_l to v_g, and the vapor-pressure from p to $p+\varDelta p$, while work equivalent to $(v_g-v_l)(p+\varDelta p)$ will be expended.

Now cool this vapor to T° and allow it to condense, under the pressure p, to its original volume v_l. The change in volume will be the same as before, with the opposite sign, but the heat evolved, w_T, will be smaller than the amount absorbed, $w_{T+\varDelta T}$, for some of the heat has been transformed into work. The work gained by the system during this process at T will be only $p(v_g-v_l)$. The total work done by the system, then, is $(p+\varDelta p)(v_g-v_l)-p(v_g-v_l)$, i.e., $\varDelta p(v_g-v_l)$.

Since w (the latent heat of evaporation at T, i.e., w_T) is the heat available at T, and the work $\varDelta p(v_g-v_l)$ has been done by the transformation of heat into work, we have (pp. 58–59),

$$\frac{\varDelta p(v_g-v_l)}{w}=\frac{\varDelta T}{T},$$

i.e.,

$$\frac{w}{T(v_g-v_l)}=\frac{\varDelta p}{\varDelta T}, \quad \text{or} \quad \frac{T(v_g-v_l)}{w}=\frac{\varDelta T}{\varDelta p}.$$

Neglecting the negligible volume v_l, and assuming the vapor behaves as an ideal gas, we would have, since

$$p(Mv)=RT, \quad \text{or} \quad v=\frac{RT}{pM}.$$

i.e.,

$$\frac{pMw}{2T^2}=\frac{\Delta p}{\Delta T} \quad \text{and} \quad \frac{2T^2}{pMw}=\frac{\Delta T}{\Delta p}.$$

It must be remembered that the latter forms are derived on the assumption of ideal conditions, and will depend in accuracy upon the holding of these conditions. The first two, on the other hand, are independent of the holding or non-holding of the gas laws.

It is necessary to remember in using these equations that 2 ($=R$) and w are in calories and p in mechanical units, while $\frac{\Delta p}{\Delta T}$ gives us the change in vapor-pressure for 1° of temperature, $\frac{\Delta T}{\Delta p}$ giving the change in boiling-point per unit of external pressure. To get a correct result, then, care must be taken with the dimensions (see p. 67). It is safest, with the first two equations, always to express the pressures as atmospheres, the volumes in liters and w in liter atmospheres, afterwards transforming the result into the units desired.

Example.—The boiling-point of ethyl iodid at 73.3 cms. is 72°.2 C., $Mw=7597$; find change in vapor-pressure for 1° C. We have

$$\frac{7597\times 73.3}{2\times(345.5)^2}=2.34 \text{ cms. Hg.}$$

In this form of the equation there can be no trouble with the dimensions, for we have calories in both numerator and denominator, so that the units used for p will be those of the result $\frac{\Delta p}{\Delta T}$, i.e., the change in pressure per degree.

20. Refraction of light.—La Place, in determining the velocity of light in various media, found the relation,

$$\frac{n_r{}^2 - 1}{d} = \text{constant for all temperatures,}$$

where n_r is the refraction of light and d is the density of the medium. For many liquids this holds true, approximately, but Gladstone and Dale found empirically a relation which holds more exactly and for many more liquids than the former. This is

$$\frac{n_r - 1}{d} = \text{constant for any one liquid.}$$

Further, in the case of a mixture, the constant is found to be equal to the sum of those for the ingredients. We have then

$$p\frac{n_r - 1}{d} = p_1\frac{n_{r1} - 1}{d_1} + p_2\frac{n_{r2} - 1}{d_2},$$

where p is equal to 100, and p_1 and p_2 represent the percentages by weight of the two ingredients. By aid of this it is possible to make an optical analysis.

Example.—An unknown mixture of amyl and ethyl alcohols gives $n_r = 1.3822$, $d = 0.8065$. What is the percentage composition of each in the mixture?

For amyl alcohol $n_{r1} = 1.4057$, $d_1 = 0.8135$; for ethyl alcohol $n_{r2} = 1.3606$, $d_2 = 0.811$; hence

$$100 \times 0.4738 = p_1 \times 0.4987 + p_2 \times 0.4501;$$

and since $p_1 + p_2 = 100$, we find $p_1 = 48.8$, $p_2 = 51.2$. By direct weighing it was found that p_1 is 48.9 and p_2 is 51.1.

This formula also holds approximately for solutions, i.e., for finding the coefficient of refraction in the solid state from that of the solution and the solvent.

21. Surface-tension. — *The surface-tension γ of a liquid is the work which is necessary to form a surface of one square centimeter in area.* Some liquids wet the walls of a glass tube, while others do not,

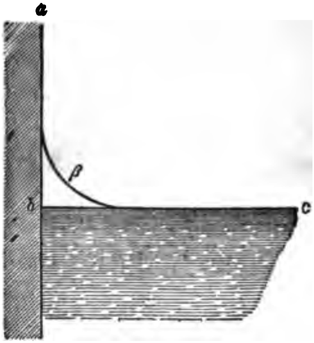

FIG. 3.

and upon this depends the shape of the surface formed. Imagine a plate of glass suspended vertically in a vessel of water, i.e., a liquid which wets the glass. The glass will then be wet as high as a (Fig. 3) and the surface abc will decrease in size by assuming the shape $a\beta c$. In doing this a certain weight of liquid will be raised. When the weight P of this portion raised is equal to the surface-tension for that length of surface, equilibrium will be established, i.e.,

$$l\gamma=P$$

or

$$\gamma=\frac{P}{l}.$$

If now instead of using a plate we use a capillary tube, with a radius equal to r, l will become $2\pi r$ and the weight of liquid raised in the tube will be

$$P=2\pi r\gamma.$$

On the other hand we have

$$P=\pi r^2hs,$$

where h is the height of the liquid in the tube (measured downward in case the liquid does not wet the walls), and s is the specific gravity, weight in grams of 1 cc., of the liquid. We have then

$$2\pi r\gamma=\pi r^2hs;$$

or

$$\gamma = 1/2hrs,$$

i.e., *the surface-tension of a liquid can be obtained from its specific gravity and the height it ascends in a capillary tube of the radius r.*

When h and r are expressed in centimeters, since s is in grams, γ will be found in terms of grams per centimeter; and multiplication by 980.1 will give γ in *dynes per centimeter;* or *ergs per square centimeter* for dynes × centimeters is equal to ergs.

22. Surface tension, molecular weight and critical temperature.—The surface-tension of a liquid has been found to depend upon the temperature and nature of the liquid, and is the basis of one of the two definitions we have of molecular weight in the liquid state. The first connection between surface-tension and molecular weight was found by Eötvös (Wied. Ann., 27, 448; 1886), who observed experimentally that the surface-tension multiplied by the 2/3 power of the product of molecular weight and specific volume is a a function of the absolute temperature. This relation, expressed mathematically, is

$$\gamma(Mv)^{\frac{2}{3}} = f(T),$$

where γ is the surface-tension in dynes, M the molecular weight, and v is the specific volume, i.e., the reciprocal of the density. Ramsay and Shields (Zeit. f. phys. Chem., 12, 431–475, 1893) expressed this relation in the form

$$\gamma V^{\frac{2}{3}} = \gamma (Mv)^{\frac{2}{3}} = k(\tau - 6),$$

where τ is the temperature reckoned downwards from the critical one, and k is a constant independent of the nature of the liquid. τ here, however, must always be greater than 35 for good results.

Ostwald explains the relation as follows: If the mole were in spherical form, the surface would be proportional to the volume raised to the power $\frac{2}{3}$, since

$$V : V_1 :: r^3 : r_1^3, \text{ and } s : s_1 :: r^2 : r_1^2.$$

We see, then, that the above law simply expresses the fact that the work necessary to form the molecular surface depends only upon the temperature, as calculated downwards from the critical one (or at least a point about 6° below this), at which the surface-tension and the work are both equal to zero. The law, in fact, is exactly analogous to the gas law $pV = RT$, for at the point from which T is reckoned the volume is equal to zero, and the volume and work above that temperature depend only on the temperature and are independent of the nature of the gas.

Using as M the value found for the gaseous state Ramsay and Shields found k for many liquids to be equal to 2.12 ergs. These liquids included C_6H_6, C_6H_5Cl, CCl_4, C_2H_6O, CS_2 and PCl_3, and many others. For other liquids k was found to be very much smaller than

2.12, which was assumed to indicate that the Mv in the formula is too small, i.e., that the molecular weight has been increased by association. Thus for H_2O $k=0.9-1.2$; for organic acids $k=0.8-1.6$; for alcohols $k=1.0-1.6$, etc. When K is the value of k as found by experiment, Ramsay and Shields assumed that the factor of association may be found from $\frac{2.12}{K}=x^{\frac{2}{3}}$, or $x=\left(\frac{2.12}{K}\right)^{\frac{3}{2}}$, where x is the factor of association.

Later work by Ramsay and Aston (Proc. Roy. Soc., 56, 162, 1894) has resulted in substituting for the above relation for x another according to which $x=\left(\frac{2.121}{k'}(1+\mu t)\right)^{\frac{3}{2}}$, when μ is a constant depending upon the nature of the liquid. *It is not as yet settled which of these relations is correct, if either, so that apparently it is not yet possible to accurately determine x from the variation from the normal value of k.* (See Bogdan, Zeit. f. phys. Chem., 57, 349-356, 1906).

An example of the use of the equations for a normal liquid will perhaps make them clearer. The radius of a capillary tube is 0.01843, at 46°, h (the height of CCl_4 in the tube) = 11.643 cm., s (the density) = 1.5420, hence $\gamma=\frac{1}{2}\,hrs.\times 980=22.9$ dynes per centimeter. Since the critical temperature = 283° and $k=2.12$, $\gamma(Mv)^{\frac{2}{3}}=492.6$ and $M=154$.

For water at 10° $K=0.87$, hence $x=3.81$ (from $\frac{2.12}{0.87}=x^{\frac{2}{3}}$), i.e., the association of water at 10° is such that its molecular weight is 3.81×18.

23. Calculation of molecular weight and critical temperature from the surface tension.—We can now define molecular weight in the liquid state; in other words, we can obtain a relation for liquids which may be used in an analogous way to the one commonly employed for gases. It is at once apparent that, according to our present use of the term, *the molecular weight of a liquid at any temperature is that weight in grams which at that temperature will occupy such a volume* Mv *(in cc.) in the formula* $\gamma(Mv)^{\frac{2}{3}}=k(\tau-d)$ *that* k *is equal approximately to* 2.12 *ergs.* For this purpose it is necessary to know the surface-tension at that temperature and the term τ, i.e., the difference between the critical temperature of the liquid and the temperature of the experiment. As it is not an easy matter to determine the critical temperature experimentally this definition is not very convenient, but it is possible to rearrange it in such a way that the knowledge of the critical temperature is not only unnecessary for the calculation of the molecular weight, but that it, also, may be calculated. If the surface-tensions and specific volumes (or densities) of any one liquid are known at two temperatures, for example, we shall have, using the reciprocal of the density in place of the specific volume,

$$\gamma_1\left(\frac{M}{d_1}\right)^{\frac{2}{3}}=k(\tau_1-6),$$

and

$$\gamma_2\left(\frac{M}{d_2}\right)^{\frac{2}{3}}=k(\tau_2-6);$$

and by subtracting the second from the first we shall obtain

$$\frac{\gamma_1\left(\frac{M}{d_1}\right)^{\frac{2}{3}}-\gamma_2\left(\frac{M}{d_2}\right)^{\frac{2}{3}}}{t_2-t_1}=k=2.12 \text{ ergs},$$

for $\tau_1-\tau_2$ is equal to (crit. temp. $-t$) $-$ (crit. temp. $-t_2$), i.e., to t_2-t_1.

This equation, however, simply expresses the fact that *the temperature coefficient of the molecular surface-tension for all liquids is approximately* 2.12 *ergs.* According to this, then, *the molecular weight in the liquid state is that weight in grams which at that temperature gives such a volume that a change in temperature of* 1° *involves an amount of surface-work, according to the above formula, equal to approximately* 2.12 *ergs.* This is similar to a definition which might be used for the gaseous state, i.e., the one expressive of the amount of external work involved by the change in temperature of 1 mole of gas 1°. This, according to p. 49, is equal to R, and we may say the molecular weight in the gaseous state is that weight in grams occupying such a volume that a temperature-change of 1° will involve the external work *R*, i.e., 2 calories, 0.0821 liter atmospheres, or 8.31×10^7 ergs.

In this way we have found a definition of molecular weight as a liquid, in which neither the critical temperature nor the constant 6 are necessary.

Knowing that *M*, as a liquid, is the same as it is as a gas, in other words, knowing *k* to be constant and independent of the temperature, even though its value is not exactly the same as the average approximate value of *k*, viz., 2.12, we can calculate the critical temperature by Ramsay and Shields' original equation. In order that the correct value of the critical temperature may be obtained from these values, Ramsay and Shields found it necessary to use the exact specific value of *k* holding for the liquid in question. An example of the whole calculation will perhaps make this clearer.

At 19°.4, for CS_2, $\gamma=33.58$, at 46°.1, $\gamma=29.41$ dynes. We have then for $\gamma(Mv)^{\frac{2}{3}}$ at the two temperatures

$$\left(\frac{76}{1.264}\right)^{\frac{2}{3}} \times 33.58 = 515.4$$

and

$$\left(\frac{76}{1.223}\right)^{\frac{2}{3}} \times 29.41 = 461.4.$$

Where 1.264 and 1.223 are the densities at the two temperatures. $\frac{\Delta(\gamma(Mv)^{\frac{2}{3}})}{\Delta T}$, i.e., $\frac{\gamma_1\left(\frac{M}{d_1}\right)^{\frac{2}{3}}-\gamma_2\left(\frac{M}{d_2}\right)^{\frac{2}{3}}}{t_2-t_1}=k$, is then equal to $\frac{515.4-461.4}{46.1-19.4}=\frac{54.0}{26.7}=2.022$, i.e., the value for k in this specific case. The critical temperature of CS_2 is then equal to $\frac{515.4}{2.022}+6+19.4=280^\circ.3$ C. There is a slight uncertainty here on account of the value 6 for the constant, as this apparently is not quite the same for all liquids; the possible error is small, however.

For τ less that 35° the formula does not seem to hold. And this is also true for associated liquids, ***only non-associated liquids allowing this determination of critical temperature to be made, for in all the other associated liquids k varies with the temperature.*** It will be seen that the original Ramsay and Shields' equation is simply an extrapolation to find from the change per degree the temperature at which the molecular surface-tension would become zero, for it must become that at the critical temperature (or 6° below it), for at that point the liquid and gas are indistinguishable and the liquid does not form a surface. Some of the critical temperatures calculated in this way by Ramsay and Shields (l.c.) are given below and will serve to show the value of this method.

CRITICAL TEMPERATURES.

Substance.	Calculated.	Observed.
Carbon disulphide, CS_2	280.3	275
		273
		277.7
		271.8
		279.6
Nitrogen peroxide, N_2O_4	226.4	171.2*
Silicon tetrachloride, $SiCl_4$	213.8	230
		221
Phosphorus trichloride, PCl_3	290.5	285.5
Benzene, C_6H_6	288	288.5
Chlorbenzene, C_6H_5Cl	359.7	360
Ethylacetic acid, $CH_3COOC_2H_5$	250.5	251
Ethyl ether, $(C_2H_5)_2O$	191.8	194.5
Carbon tetrachloride, CCl_4	282.1	283.2
Paraldehyde, $C_6H_{12}O_3$	310.5	

* The calculated value here does not account for the dissociation into $2NO_2$. The value 171.2 is the critical temperature of a mixture of N_2O_4 and NO_2.

In the tables which follow are collected some of the molecular weights, calculated by aid of the surface-tension from capillary rise and the Ramsay and Shields formula, for both so-called associated and non-associated liquids.

NON-ASSOCIATED LIQUIDS.

t	γ (dynes per cm.)	$(Mv)^{\frac{2}{3}}$.	$x \times M$
	CS_2. Carbon disulphide.		
19°.4	33.58	515.4	
46°.1	29.41	461.4	1.07×76
	N_2O_4. Nitrogen peroxide.		
1°.6	29.52	461.0	
19°.8	26.56	423.5	1.01×92
	$SiCl_4$. Silicon tetrachloride.		
18°.9	16.31	383.9	
45°.5	13.66	329.8	1.06×169.6
	PCl_3. Phosphorus trichloride.		
16°.4	28.71	562.3	
46°.2	24.91	499.8	1.02×137.2

CCl_4. Carbon tetrachloride	1.01×153.6
C_6H_6. Benzene	1.01×78
$(C_2H_5)_2O$. Ethyl ether	0.99×74
C_6H_5Cl. Chlorbenzene	1.03×112.4
$C_6H_5NH_2$. Aniline	1.05×93
C_5H_5N. Pyridin	0.93×79
Hg.* Mercury (liquid)	171

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* Kistjakowski, J. russ. phys. chem. Ges., 34, pp. 70–90. This value is found from surface-tension assuming the critical temperature to be about 700°C

ASSOCIATED LIQUIDS BY FORMULA $x=\left(\frac{2.12}{K}\right)^{\frac{3}{2}}$.

ALCOHOLS.

Name.	16–46° $x \times M$	46–78° $x \times M$	78–132° $x \times M$
Methyl.	3.43×32	3.24×32	2.89×32
Ethyl.	2.74×46	2.43×46	1.97×46
Propyl.	2.25×60	2.31×60	
Isopropyl.	2.86×60	2.72×60	
Butyl.	1.94×74	1.72×74	1.76×74
Isobutyl.	1.95×74	1.86×74	1.64×74
Amyl.	1.97×88	1.69×88	1.57×88
Allyl.	1.88×58	1.86×58	
Glycol.	2.92×62	2.48×62	2.12×62

ACIDS.

Name.	16–46° $x \times M$	46–78° $x \times M$	78–132° $x \times M$
Formic.	3.61×46	3.13×46	
Acetic.	3.62×60	3.32×60	2.77×60
Propionic.	1.77×74	1.78×74	1.88×74
Butyric.	1.58×88	1.73×88	1.69×88
Isobutyric.	1.45×88	1.82×88	1.73×88
Valerianic.	1.36×102	1.37×102	1.70×102
Capronic.	1.46×116	1.47×116	1.49×116

WATER.

t	γ	$\gamma(Mv)^{\frac{2}{3}}$	$x \times M$
0°	73.21	502.9	3.81×18
10°	71.94	494.2	3.68×18
20°	70.60	485.3	3.44×18
30°	69.10	476.0	3.18×18
40°	67.50	466.0	3.13×18
50°	65.98	456.7	3.00×18
60°	64.27	446.4	2.96×18
70°	62.55	436.0	2.83×18
80°	60.84	425.9	2.79×18
90°	58.92	414.3	2.66×18
100°	57.15	403.7	2.61×18
110°	55.25	392.3	2.47×18
120°	53.30	380.4	2.47×18
130°	51.44	369.2	2.32×18
140°	49.42	356.8	

FACTOR OF ASSOCIATION BY FORMULA $x = \left\{\frac{2.121}{k}(1+\mu t)\right\}^{\frac{3}{2}}$.

Methyl Alcohol.		Ethyl Alcohol.		Water.	
t	x	t	x	t	x
−89.8	2.65	−89.8	2.03	0	1.707
+20	2.32	+20	1.65	20	1.644
70	2.17	40	1.59	40	1.582
90	2.11	60	1.52	60	1.523
110	2.06	80	1.46	80	1.463
130	2.00	100	1.39	100	1.405
150	1.94	120	1.33	120	1.346
170	1.89	140	1.27	140	1.289
180	1.86	160	1.21		
190	1.83	180	1.15		
200	1.81	200	1.09		
210	1.78	210	1.06		
220	1.75	220	1.03		
		230	1.00		

Measurements have also been made by Bottomley (Trans. Chem. Soc. 83–84, 1421–1425, 1904) in this way of the factors of association of fused salts, using the equation $x = \left\{\frac{2.12}{K}\right\}^{\frac{3}{2}}$. His results are as follows:

POTASSIUM NITRATE, KNO_3.

t	γ	$\gamma(Mv)^{\frac{2}{3}}$	K	$x \times M$
338	109.8	1571	0.471	9.55×101
406	105.8	1539		
349	106.4	1521	0.584	7.49×101
414	100.7	1485		
341	106.4	1551	0.485	9.145×101
407	104.6	1519		

SODIUM NITRATE, $NaNO_3$.

t	γ	$\gamma(Mv)^{\frac{2}{3}}$	K	$x \times M$
339 405	106.4 101.8	1374 1308	0.500	8.73×85
329 405	110.8 106.5	1398 1369	0.381	13.13×85
344	111.0	1403	0.453	10.17×85

For liquefied gases Baly and Donnan (Trans. Chem., 81, 907–923, 1902) found slightly lower values for k than 2.12. Their values are:

Substance.	$k = \frac{\Delta(\gamma(Mv)^{\frac{2}{3}})}{\Delta t}$
Oxygen	1.917
Nitrogen	2.002
Argon	2.020
Carbon monoxide	1.996

Oxygen and nitrogen apparently cut the temperature axis at points which are practically coincident with their critical temperatures, while argon and carbon monoxide cut the axis at temperatures lower than their critical values (9° for argon and 5° for carbon monoxide.)

For liquefied carbon dioxide Verschaffelt (Verslage Kon. Akad. van Wetenschappen, 4, 74, 1895–96) has found the value $k = 2.222$, and for nitrous oxide, $k = 2.198$, in both cases the temperature axis being cut 6° below the critical value.

These results, together with the one for liquid mercury given above, show that this method in its approximate form (i.e., for molecular weight determinations) is applicable to all liquids. It has been shown by Ramsay to hold also for liquid mixtures.

23a. Calculation of the molecular weight and critical temperature by the aid of the weight of a falling drop.—Morgan and Stevenson (Jour. Am. Chem. Soc., 30, 360–376, 1908) from careful measurements of the volumes of a single drop falling from a capillary tip, beveled at an angle of 45°, have shown that the weight of the falling drop, from any one such tip, can be employed in place of the surface-tension in the Ramsay and Shields formulas for the calculation of the molecular weights and critical temperatures. The results of this method they found to be considerably better than those calculated from the measurements of capillary rise by Ramsay and Shields, and equal in accuracy to those from the capillary rise, under like, saturated air, conditions, as found by Renard and Guye (J. Chem. Phys., 5, 81, 1907).

Morgan and Higgins (Jour. Am. Chem. Soc. 30, 1055–1068, 1908), in continuing the work, were able to refine the method to such an extent that the mean error of Morgan and Stevenson, which amounted to ±0.4% to 0.5%, was reduced to a few hundredths of 1%. Naturally, their results for drop weight led to still better values for both molecular weight and critical temperature, as is shown by the following facts brought out by their work:

(1) Falling drop-weight leads more accurately to *true* relative surface-tension than does capillary rise, and fulfills the equations especially designed for capillary rise results better than they themselves do.

(2) The molecular temperature coefficient, $k_{\text{temp.}}$, corresponding to Ramsay and Shields' k, and defined by the equation,

$$k_{\text{temp.}} = \frac{w_1\left(\frac{M}{d_1}\right)^{\frac{2}{3}} - w_2\left(\frac{M}{d_2}\right)^{\frac{2}{3}}}{t_1 - t_2},$$

where w_1 and w_2 are the falling drop weights at t_1 and t_2, is practically invariable ($2.5694 \pm 0.05\%$, for a certain tip), as against a mean variation in k of $\pm 3.2\%$ according to Ramsay and Shields, and of $\pm 1.56\%$ according to Renard and Guye's results from capillary rise.

This constancy in the value of $k_{\text{temp.}}$ for all the non-associated liqudis used, and presumably for all others as well, enables one to calculate the critical temperature of any non-associated liquid from a falling drop-weight (from that tip) at any one temperature, without first finding, as Ramsay and Shields were forced to do, the exact value of $k_{\text{temp.}}$ for that specific liquid; for the value so found for any other non-associated liquid can be used. It also, in addition to being simpler experimentally, leads to more accurate values of critical temperature, as will be observed in the cases of aniline and quinoline in the table below.

Another effect of the practically invariable value of $k_{\text{temp.}}$, for all the non-associated liquids, is to make the drop method the most accurate one known for the determination of molecular weight, with the exception of the one adapted to permanent gases and dependent upon the density. The relation of the percentage error in M to the percentage error in the $k_{temp.}$ (or k) from which it is calculated, shows at a glance the error in the method, and can be readily found by differentiating with respect to M and $k_{temp.}$, the above equation defining the latter, and then dividing the result by the original equation. Performing this operation we find

$$\frac{dM}{M} = \frac{3}{2}\frac{dk_{temp.}}{k_{temp.}},$$

i.e., the percentage error in M is 3/2 the percentage error in the $k_{temp.}$ from which it is calculated. From the table below it will be seen that the difference between the highest value of $k_{temp.}$ (quinoline) and the lowest (carbon tetrachloride or pyridine) is but 0.3%, hence the error in M for the liquid giving the maximum $k_{temp.}$, when calculated from the $k_{temp.}$ of the liquid giving the minimum $k_{temp.}$ would only be 0.45%; while using the mean value of $k_{temp.}$ the molecular weight of the quinoline would be burdened with an error equal to but ±0.2%; and the error in the M for any of the other five liquids would only amount to 1 or 2 hundredths of 1%, either by use of the mean $k_{temp.}$ or of any of the specific values.

In the following table is given a summary of the results of Morgan and Higgins. In the second column is given the value of $k_{temp.}$ as calculated from the experimental drop-weights at two temperatures (one about 25°, the other about 75°); in the third is the critical temperature calculated from the Ramsay and Shields formula, after substituting w for γ; in the fourth are the k values as found by Renard and Guye, from the capillary rise (these are from the smoothed curve); in the fifth are the critical temperatures calculated from these; and, finally, in the sixth are the experimentally observed values of critical temperature.

Liquid.	$k_{temp.}$	Crit. temp.	$k_{R\&G}$	Crit. temp.	Obs. crit. temp.
Benzene	2.569	288.4	2.12	287.7	ca. 288
Chlorbenzene	2.569	359.5	2.10	357.7	ca. 360
Carbon tetrachloride	2.567	285.2	2.19	278.0	ca. 284
Pyridine	2.567	347.0	2.07	346.2	ca. 344
Aniline.	2.569	425.8	2.01	448.6	ca. 426
Quinoline	2.575	520.4	2.21	496.2	> 520

The method in the form employed by Morgan and Stevenson, and Morgan and Higgins, it must be understood, is most decidedly not adapted to general laboratory use, as are the vapor density methods, for example, for it requires much experience and manipulative skill. A drop-weight method, however, that is adapted to such general purposes is shortly to be described by Morgan which leads to very accurate results, and is so simple to operate and so rapid that it is admirably adapted to the needs of the ordinary worker.

It has been shown by Higgins (Jour. Am. Chem. Soc. 30, 1069–1073, 1908), as the result of the work of Morgan and Higgins, for a number of non-associated liquids, that in corresponding states, i.e., at equal distances from the boiling point, the molecular drop *volume*, from any one tip, varies inversely as the absolute temperature. In other words, we have, similar to the law of Trouton,* the relation,

$$\frac{Mv_{F.D.}}{T} = \text{constant}, = K_{B.P.-x},$$

where M is the molecular weight, $v_{F.D.}$ the volume of a falling drop from any one, beveled, tip, at the absolute temperature T. Or, eliminating the constant for two liquids,

$$\frac{Mv_{F.D.}}{M'v'_{F.D.}} = \frac{T-x^\circ}{T'-x^\circ},$$

T and T' being the absolute boiling-points, and x (the number of degrees T is below the absolute boiling point) having any value.

The values of the constant in the first equation ($K_{B.P.-x}$) are approximately, $K_{B.P.-0}=660$, $K_{B.P.-10}=713$, $K_{B.P.-20}=766$, $K_{B.P.-30}=824$, $K_{B.P.-40}=880$.

Since from the above $v_{F.D.} = \frac{T}{M}K_{B.P.-x}$, it is possible from the knowledge of the molecular weight of a non-associated liquid and its boiling-point, to calculate its drop volume (and hence its surface-tension) at any temperature. Hence we may write the Ramsay and Shields formula,

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* See also Kistiakovski (Z. f. Elektrochem., 12, 513–514, and 615, 1906), the molecular capillary constant (i.e., height of ascension in tube of unit bore) varies with the absolute boiling-point.

$$d\frac{T}{M}K_{\text{B.P.}-x}\left(\frac{M}{d}\right)^{\frac{2}{3}}=k_{\text{temp.}}(\tau-6),$$

where d is the density at the absolute temperature T, and find the critical temperature $(\tau+T-273)$. In addition to this, it is possible by use of the Nernst equation (see Bingham, Jour. Am. Chem. Soc., 28, 717, 1906), at the boiling-point, where the vapor-pressure is 1 atmosphere, knowing the critical temperature to find the critical pressure, and then knowing this to calculate the vapor-pressure at any temperature. And when both critical temperature and critical pressure are known van der Waal's constants a and b can be calculated.

In short, then, it is possible by the above relations, knowing the density and the constants, molecular weight, drop volume, from any one tip, at any temperature, to find the critical temperature, critical pressure, vapor-pressure at any temperature, and the value of "a" and "b."

In the table at the top of page 98 are given some calculated critical temperatures, obtained by solving the equation in each case for a temperature 20° below the boiling-point ($K_{\text{B.P.}-20}=776$; $k_{\text{temp.}}=2.569$).

24. The molecular weight in the liquid state.—It will be seen from what has been said above, that liquids

				Critical Temperature	
Liquid	Molecular weight	Boiling point	Density 20° below B. P.	Calculated	Experimental
Chloroform	119.4	61.2	1.4464	262.4	260
Chlorbenzene	112.4	132.0	1.0063	356.5	360
Ethylidene chloride	98.9	59.2	1.1420	255.7	255
Toluene	92.0	110.0	0.7981	320.1	321
Pyridine	79.0	114.5	0.9067	347.7	345

may be divided into two groups—those which are normal, and lead in certain equations to identical, or nearly identical, constants—and those which, in the same equations, lead to different ones, usually variable with the temperature. This is shown very clearly by the Nernst-Bingham forms of Trouton's law, by the relations of Mills and Crompton, by the relation of Young (Phil. Mag., V, 50, 291, 1900; that the ratio of the actual density at the critical point to the theoretical density, as calculated for a perfect gas, is the same for all substances), by the relations of Ramsay and Shields, and of Morgan and Stevenson, and by several others.

In accord with this difference in behavior it is customary to divide liquids into those which are normal, or *non-associated*, and those which are *associated;* the behavior of the latter being assumed, according to the nature of the method used, to be due to the polymerization or association of the liquid, or to the energy involved in reducing the existing larger molecular weight to that which it possesses as a gas.

Although all the methods agree, within their limits of error, in the selection of the liquids which are associated, only the relation of Ramsay and Shields can be used to calculate the extent of the polymerization, i.e., of the factor of association. And even the correctness of this is still too much in doubt to make the results more than a rough approximation (see Bogdan, Zeit. f. phys. Chem., 57, 349–356, 1906).

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CHAPTER IV.

THE SOLID STATE.

25. Remarks.—A solid is a substance which possesses a form of its own, i.e., its shape is not dependent upon that of the vessel in which it is.

Just as we find that a substance contains less energy in the liquid state than it does as a gas, so we find that a solid contains less energy than a liquid, i.e., in going into the liquid state, it absorbs heat-energy.

26. Atomic heat. Law of Dulong and Petit.—*The atomic weight of all elements have approximately the same capacity for heat.* A few elements have been found to give different values, but in general for all elements (except boron, silicon, and carbon) we find that

$$\text{atomic heat} = \text{atomic weight} \times \text{specific heat} = 6.34.$$

This is the *law of Dulong and Petit.*

Lewis (J. Am. Chem. Soc., 29, 1165–1168, 1907) has recently announced the following law: *Within the limits of experimental error, the atomic heat at constant volume, at 20°, is the same for all solid elements whose atomic weights are greater than that of potassium, and is equal to* 5.9. The relation of this specific heat at constant volume and that usually experimentally determined, at constant pressure, is given by the formula,

$$C_p - C_v = \frac{T\beta^2 V}{41.78\alpha},$$

where T is the absolute temperature, β the coefficient of thermal expansion, α the compressibility coefficient, C_p and C_v are the specific heats times atomic weights, and V the atomic volume, i.e., atomic weight times specific volume.

At first glance it would seem that the law of Dulong and Petit would enable us to define the molecular weight in the solid state, since the sum of the atomic weights, i.e., the molecular weight, multiplied by the specific heat of the compound should give approximately the same value as is obtained when 6.34 is multiplied by the number of atomic weights in the former. But a moment's thought will show that this relation is only of value in that it insures uniformity in the choice of the atomic weight to be used, and can have nothing to do with fixing the molecular weight of the compound. Thus analysis shows the existence of two chlorides of mercury, the simplest formulas of which are HgCl an $HgCl_2$, but the application of the law of Dulong an Petit does not enable us to state whether the formul in the solid state are HgCl and $HgCl_2$ or Hg_2Cl_2 ar Hg_2Cl_4, any more than the analytical result does.* is only because the formulas Hg_2Cl_2 and $HgCl_2$ (n Hg_2Cl_4) are found under certain conditions in the gaseo state that they are *assumed* in the solid state.

In all reactions involving solids, then, it is only t actual weight of the reacting substances that is essenti and the very fact that we cannot define molecular weig in the solid state shows its utter lack of chemical physical influence. If this at any time should be chang and it appear that the molecular weight does exert influence experimentally, naturally all our difficu would disappear, for then a definition could at once derived from observations of this influence.

27. **Changes in the state of aggregation.**—The mo important process concerning solids, for our purpose, their formation from the liquid state, or the formati of the liquid state from them.

If a liquid is cooled very carefully it is possible reduce its temperature below the solidifying-point an yet have no solid formed. If the crystal of the su stance is then thrown in, crystallization takes place immediately, and the temperature rises rapidly to the true solidifying-point. Besides this change in temperature we have also one in volume, since the specific volume in the one state differs from that in the other.

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* For HgCl we have (200+35.5) 0.052=12.25, for Hg_2Cl_2 (400+71 0.052=24.5; while 2×6.34=12.68 and 4×6.34=25.36.

When a gas condenses and goes into the liquid state heat is given off. In the same way heat is also given off when a solid is formed from a liquid, and this is the cause of the rise in the temperature spoken of above. The heat which is liberated by a liquid solidifying (or absorbed by a solid liquefying) is called, for 1 gram of substance, *the latent heat of solidification* (*or fusion*). This heat, referring to 1 mole of substance (heat for the molecular weight), is called *the molecular heat of solidification* (*fusion*). The effect of pressure upon the solidifying-point may be derived by the consideration of a thermodynamic cycle, just as we did for liquids, p. 73.

Starting with 1 gram of a liquid at the temperature T, occupying the volume v, and under its own vapor-pressure p, cool ΔT°, i.e., to $T-\Delta T$ and assume it to be completely transformed into the solid state. During this process an amount of heat equal to w' calories at the temperature $T-\Delta T$ will be evolved, the volume will change from v_l to v_s, the vapor-pressure from p to $p-\Delta p$, and an amount of work equal to $(v_l-v_s)(p-\Delta p)$ will be involved.

Now heat the solid thus obtained to T° and allow it to melt at the pressure p to form the original volume v_l. This change in volume will be the same as the previous one, except that it has the opposite sign. The heat, w, involved at $T°$, however, will be different from that previously involved at $T-\Delta T$, and the difference will be equivalent to the total amount of external work done by or upon the system. The work during this stage will be $p(v_l-v_s)$. The total work of the whole process, i.e., after the original state is once more attained, is $\Delta p(v_l-v_s)$, i.e., $p(v_l-v_s)-(p-\Delta p)(v_l-v_s)$, and consequently by the second law (pages 58–59), since w is the heat available at $T°$ to do work.

$$\frac{\Delta p(v_l-v_s)}{w}=\frac{\Delta T}{T},$$

or

$$\frac{\Delta p}{\Delta T}=\frac{w}{T(v_l-v_s)} \quad \text{or} \quad \frac{\Delta T}{\Delta p}=\frac{T(v_l-v_s)}{w},$$

v_l being the specific volume of the liquid, v_s that of the solid substance, and w the latent heat of fusion for 1 gram at $T°$.

This formula is not only of use in case of a change in the state of aggregation, but also for any *reversible* change, for example, that taking place between allotropic forms of the same substance. Thus at 95°.6 C. the rhombic form of sulphur is transformed into the monoclinic form. The reaction is perfectly reversible, an increase of heat increasing the amount of the monoclinic form, a decrease increasing that of the rhombic. The change in volume being 0.014 cm. and the heat of transformation 2.52 cals., both per gram, we have,

$$\frac{\Delta T}{\Delta p}=\frac{T\Delta v}{w}=\frac{(273+95.6)0.000014}{2.52\times 0.041}=0^{\circ}.05 \text{ per atmos.}$$

where the term w is transformed into liter-asmosphere v into liters, and the result given in degrees per atmosphere; i.e., an increase of pressure of 1 atmosphere increases the transformation temperature by 0°.05, a result which agrees well with the experimental value.

If the specific volume of the solid is greater than that of the liquid, i.e., if the solid floats upon the liquid (ice in water), the freezing-point will be depressed by pressure. If, on the other hand, the specific volume of the solid is less than that of the liquid, i.e., if the solid sinks, the solidifying-point will be raised by increased pressure. In the former case the pressure will tend to keep the substance in the liquid form, since that has the smaller volume, and a lower temperature will be necessary to produce the solid. In the latter case the formation of the solid will be aided by the pressure, and consequently the temperature need not be lowered to such an extent. This is simply another application of the principle of Le Chatelier (page 33).

The actual effect of pressure upon the solidifying-point, however, is not large. Thus an increase of pressure up to 8.1 atmospheres depresses the freezing-point of water but 0.059° C.

The above equations give us also the heat of sublimation, i.e., of the direct transition from the solid to the gaseous state, if the volumes represent those of solid and gas; or the volume of gas alone may be used by substituting for v the value found from $pV=RT$, changing w to Mw, i.e., the gram heat to the molecular heat, and v to $Mv=V$.

The sublimation-pressure of a solid is to be considered just as the vapor-pressure (i.e., evaporation-pressure) of a liquid. It is noticed that some solids sublime while others melt and evaporate. The reason for this difference is the fact that when the sublimation-pressure exceeds the pressure of the atmosphere sublimation takes place and thus keeps the solid from melting. When heated in closed vessels, however, the pressure becomes great enough to prevent continuous sublimation, so that after a small portion sublimes and raises the pressure, the remainder will melt. This can be shown experimentally by heating iodine, which usually sublimes and does not melt, under sulphuric acid, the pressure of which prevents sublimation and allows fusion to take place.

Since at the solidifying- or freezing-point the solid and liquid exist in contact in all proportions, the vapor-pressure of the solid must be equal to that of the liquid, both at the same temperature. That this must be so follows from the following process: Imagine in the annular-shaped vessel, Fig. 4, water at *b*, ice at *a*, and the vapor

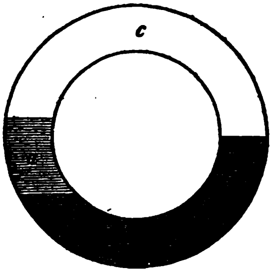

FIG. 4.

of the two at *c*: all being at the temperature of 0° C. If the vapor-pressure over the water at *b* is greater than that over the ice at *a*, a distillation from *b* to *a* must take place. By the evaporation at *b* heat will be absorbed, and by the condensation of this vapor to ice at *a*, under the diminished pressure, heat will be liberated. A layer of ice will thus be formed at *b*, while the heat liberated will melt an amount of ice at *a*. We would have, then, an exchange of heat at the same temperature. If this were possible, perpetual motion would be possible; since, however, the latter is impossible, the vapor-pressure of the solid must be the same as that of the liquid, both having the same temperature.

The latent heat of fusion of a solid varies with the temperature just as does that of evaporation, and the expression for it may be derived in a similar manner. The difference in the external work involved in these changes is so slight that we may consider them equal. (1) One gram of solid is allowed to melt at its fusion temperature T by which the heat absorbed is w_T, and the resulting liquid heated to $T+t$, which absorbs the heat c_lt. (2) The gram of solid is first heated to $T+t$, which absorbs the heat c_st, and then allowed to melt, absorbing the heat w_{T+t}. Since the loss in energy by the two processes must be the same, we have

$$-(c_lt+w\ )=-(c_st+w_{T+t})$$

and

$$c_l-t_s=\frac{w_{T+t}-w_T}{t}=\frac{\Delta w}{\Delta T}.$$

The latent heat of fusion increases per degree, around a certain temperature, by an amount equal to the specific heat as a liquid minus the specific heat as a solid, both at that temperature.

By this we see that if the specific heat of the solid is larger than that of the liquid state, the heat of fusion decreases with increasing temperature.

In the case of H_2O $c_l=1$, $c_s=0.5$; hence $\frac{\Delta w}{\Delta T}=0.5$, i.e., the heat of fusion changes by 0.5 cals. for a change in temperature of 1°. In this case there is a decrease in heat with a decrease of temperature, i.e., temperature and heat increase together. If the sign of $\frac{\Delta w}{\Delta T}$ were minus this relation would be just the contrary, and the heat would decrease with an increase in temperature.

The latent heat of fusion for water, then, is

$$w_w = 80 + 0.5t.$$

Thus when freezing at -4°, caused by pressure of 530 atmospheres, $w_w = 78$.

From the relation $\Delta T(c_l - c_s) = \Delta w$ we can find the change in temperature necessary to reduce the latent heat of fusion to zero, i.e., the temperature at which it passes through the value zero and changes its sign. Thus for water, since $w = 80$ at 0°, it would be necessary to lower the temperature of solidification $\Delta T = 160^\circ$ to get zero heat of fusion, i.e., to make Δw equal to 80°, for $c_l - c_s = 0.5$.

Tammann (Kristallisieren und Schmelzen, p. 45) gives a list of *absolute* temperatures at which w_f becomes zero, which are derived in this way. Thus we have, for example,

Substance.	Absolute temperature at which $w_f = 0$.
Naphthalene	38
$Na_2S_2O_3 \cdot 5H_2O$	15
Phosphorus	131
$CaCl_2 \cdot 6H_2O$	113
Diphenylamine	130

The variation in the latent heat of *sublimation* with the temperature can be calculated by the formula used for the variation of the heat of vaporization, the specific heat of the solid being substituted for that of the liquid (76).

Although in the derivation on page 103 we assumed that *all* the liquid solidifies at the temperature $T-\Delta T$, this could not happen instantaneously. There is, in fact, a definite relationship between the number of degrees of overcooling and the fraction of liquid which as a result separates at once to form solid. That this must be so is obvious after a moment's thought. Since the freezing-point of a liquid is that point at which solid and liquid can exist together in all proportions, it must be the final point attained after any overcooling which leaves a portion of the liquid. According to this, then, only as much solid can separate after a definite overcooling as will just bring the system from its overcooled point to its freezing-point; in other words, the heat evolved must be equal to the heat necessary to raise the temperature of the system to the freezing-point. If f is the *fraction* of 1 gram of liquid which is separated as solid, the heat evolved will be fw', while the heat necessary to raise the system to be freezing point is $c\Delta t$. We must have, then,

$$fw'=c\Delta t,$$

or

$$f=\Delta t\frac{c}{w'}.$$

The term c here, although referring in reality to the average specific heat of the system liquid-solid between the temperatures t and Δt may be replaced by the specific heat of the liquid at the freezing-point c_l; and w', which really refers to the latent heat at the temperature $t-\Delta t$ may be replaced by the latent heat at t°, w. This possibility is due to the fact that the change in the specific heat of the system, as well as the variation in the latent heat per degree, depends upon the specific heats in the two states, so that the ratio $\frac{c}{w'}$ remains constant no matter what the amount of liquid transformed into the solid state. If, for example, the fraction f of liquid solidifies, owing to the overcooling Δt, we have as specific heat of the system $(1-f)c_l+fc_s$, and the heat necessary to raise it Δt° is $\Delta t[(1-f)c_l+fc_s]$. The heat delivered by the system at $t-\Delta t$, however, according to page 108, is $f[w-\Delta t(c_l-c_s)]$ cals., where w is the heat of fusion a t°, and f is the fraction of the amount of liquid which becomes solid and thus gives out f times w cals. The heat delivered by the solidification at $t-\Delta t$ must be just sufficient to raise the temperature Δt° to t, hence we have

$$\Delta t[(1-f)c_l+fc_s]=f[w-\Delta t(c_t-c_s)],$$

and, by simplification,

$$f=\Delta t\frac{c}{w}\cdot$$

The fraction of liquid separating as solid is equal to the degrees of overcooling multiplied by the specific heat of *the liquid over the latent heat of fusion, both at the fusion emperature.* The specific heat in the liquid state and the latent heat at the freezing-point may thus be used throughout to give the fraction of liquid separated. A specific example will perhaps make this clearer. For water we have $c_l=1$, $c_s=0.5$, while w at 0° is 80 cals. When overcooled to −10° C. how much of the liquid is separated as ice?

$$f=\Delta t\frac{c_l}{w}=10\tfrac{1}{80}=\tfrac{1}{8},$$

i.e., 125 grams of liquid from each liter will solidify. To check this value we shall calculate the specific heat of the system and see that the amount of heat given out at −10° is just sufficient to raise the temperature to 0°. The specific heat of the system is $(1-\frac{1}{8})1+\frac{1}{8}\times.5$, i.e., $\frac{7.5}{8}$. The latent heat at −10° is $(80-10\times0.5)=75$ cals. The ratio, specific heat to latent heat, then, as before, is

$$\frac{\frac{7.5}{8}}{75}=\frac{1}{80}.$$

If a large amount of liquid solute is present, c_l in the above equation must represent the specific heat of the solution. This can be found from the relation,

$$c_{\text{solution}}=\frac{\text{w'g't solute}\times c_{\text{solute}}+\text{w'g't solvent}\times c_{\text{solvent}}}{\text{w'g't solvent}+\text{w'g't solute}}.$$

For strong solutions, we have

$$f = \Delta t \frac{c_{\text{solution}}}{w};$$

while for weak solutions,

$$f = \Delta t \frac{c_{\text{solvent}}}{w}.$$

By the law of the conservation of energy the heat of *sublimation* (pp. 106 and 109) at the melting-point must naturally be equal to the sum of the heat of fusion and the heat of evaporation, i.e., the same energy difference must exist between solid and gas, whether the solid goes directly into gas, or first into liquid and then into gas, so long as the temperature is the same. We have then,

$$w_s = w_f + w_e = T\frac{\Delta p}{\Delta T}v_g,$$

or, since for Mw we have $Mv_g = V_g$,

$$Mw_s = M(w_f + w_e) = T\frac{\Delta p}{\Delta T}V_g,$$

where p is the vapor-pressure of the solid.

But

$$Mw_e = T\frac{\Delta P}{\Delta T}V_g,$$

where P is the vapor-pressure of the liquid.

By combination, then, we obtain, by aid of (1),

$$Mw_f = TV_0\left(\frac{\Delta p}{\Delta T}-\frac{\Delta P}{\Delta T}\right) = \frac{RT^2}{p'}\left(\frac{\Delta p}{\Delta T}-\frac{\Delta P}{\Delta T}\right),$$

where p' is the vapor-pressure for both liquid and solid at the melting-point. As an example of the use of this formula we shall calculate the difference in the temperature coefficients of the vapor-pressure in the solid and liquid states. For benzene at the fusion temperature 5°.6 the heat of fusion is 30.18 cals. and p is equal to 35.5 mm., and we have

$$M\ 30.18 = \frac{RT^2}{p}\left(\frac{\Delta p}{\Delta T}-\frac{\Delta P}{\Delta T}\right),$$

$$\frac{\Delta p}{\Delta T}-\frac{\Delta P}{\Delta T} = \frac{30.18 \times 35.5 \times 78}{2(273+5.6)^2} = 0.538 \text{ mm.}$$

while by experiment it is found to be

$$\frac{\Delta p}{\Delta T}-\frac{\Delta P}{\Delta T} = 2.428 - 1.905 = 0.523 \text{ mm.}$$

The variation in the heat of sublimation with the temperature can be found readily from the above relations, remembering that

$$\frac{\Delta w_f}{\Delta T} = c_l - c_s \quad \text{and} \quad \frac{\Delta w_e}{\Delta T} = c_p - c_l,$$

as follows:

$$\frac{\Delta w_s}{\Delta T} = \frac{\Delta w_f}{\Delta T} + \frac{\Delta w_e}{\Delta T} = c_l - c_s + c_p - c_l = c_p - c_s.$$

The variation of the heat of sublimation per degree is equal to the difference between the specific heats as a gas and as a solid. This relation can also be derived directly from a thermodynamic cycle as were those for evaporation and fusion (pp. 74 and 108).

CHAPTER V.

THE PHASE RULE.*

28. Object of the phase rule.—Thus far we have considered the three possible states of aggregation, gases liquids, and solids, as systems existing alone, and at mos have studied the quantitative relations of these as such and their mutual transformations the one into the other Although all the *quantitative* relations possible are thu expressed, there are certain further *qualitative* relations regulating the equilibrium existing between the states which have not been touched upon. These relations ar summed up in the phase rule, as derived by Willard Gibbs which is the subject of this chapter.

In order to understand quite clearly the object of thi rule, the following systems may be considered: Whe water is placed in the Torricellian vacuum of a baromete the mercury is depressed and the depression increase with the temperature of the water. At any one temperature, however, the pressure is independent of the amoun of water present. Water and its vapor, then, can exi permanently side by side, i.e., in equilibrium when, at a given temperature, the pressure has a definite value. If a salt solution is substituted for the water, however, the relation is different. It is true that an increase of temperature still increases the pressure; but the pressure is no longer independent of the volume, for the greater the volume (i.e., the greater the amount of water forming water-vapor), the smaller is the pressure. The presence of solid salt, however, in contact with the solution, causes the pressure to remain constant, irrespective of the actual volume.

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* For further details on this subject see Findlay's "The Phase Ru and its Applications," of which I have made free use in this Chapter.

Further, by cooling water ice is formed, and so long as this is present with the water the application (or removal) of heat varies neither the temperature nor the vapor-pressure of the system. Thus it is only at one definite pressure and one definite temperature that ice, water and water-vapor can exist together in equilibrium. In the case of a salt solution, on the other hand, we may have ice in contact with the solution at different temperatures and pressures.

The phase rule enables us to decide the necessary conditions for equilibrium in cases of this sort, as well as in all others where an analogous equilibrium is possible.

29. **The phase rule.**—Before formulating the law itself it will be necessary to define the terms used by it. A *phase* is a physically distinct, homogeneous and mechanically separable portion of the system; it need not, however,

be chemically simple. A gaseous mixture or a solution may form a phase; but a heterogeneous mixture of solids represents as many phases as there are substances present. The dissociation of calcium carbonate thus gives two solid phases, calcium carbonate and calcium oxide, and one gaseous phase, carbon dioxide. It is to be remembered that but one gaseous phase may be present, for all gases are miscible in all proportions. The *components* of a system are those constituents which in concentration can undergo *independent* variation in the different phases. Thus, in the above example, water, not hydrogen and oxygen, is the component; and although calcium carbonate, oxide and carbon dioxide are constituents of the equilibrium, only two need be considered as components, for the amount of the other is not independent of the amounts of these, but dependent according to the chemical reaction

$$CaCO_3 = CaO + CO_2.$$

Thus taking CaO and CO_2 as the components, the composition of each phase can be easily expressed.

In general, the components are to be chosen from the constituents at equilibrium, and are chosen as the *smallest number* of independently variable constituents necessary to express the composition of each phase participating in the equilibrium, zero and negative quantities of the components being permissible.

The **degree of freedom** is the number of variable factors, temperature, pressure and concentration of the components which must be arbitrarily fixed in order that the condition of the system may be perfectly defined. Thus a gas has two degrees of freedom, for it is necessary to fix two of the conditions, temperature, pressure or volume, to define it; a liquid and its vapor has but one, for equilibrium at a certain temperature exists only at a certain pressure; while a system of a liquid, its solid and gas, has no degree of freedom, for equilibrium can only exist at a certain temperature and pressure, for otherwise one of the phases will disappear.

Gibbs' phase rule defines the condition of equilibrium by the relation between the number of coexisting phases and components. *According to it a system made up of n components in n+2 phases can only exist when pressure temperature and composition have definite fixed values; a system of n components in n+1 phases can exist so long as only one of the factors varies; and a system of n components in n phases can exist while two of the factors vary. In other words, the degree of freedom is expressed by the equation*

$$P+F=C+2, \quad \text{or} \quad F=C+2-P$$

where P designates the number of phases, C the number of components, and F the degree of freedom.

Since in the equilibrium of $CaCO_3$ we have two components (CaO and CO_2) and three phases (two solid, CaO and $CaCO_3$, and 1 gaseous, CO_2) the degree of freedom is $2+2-3=1$. This is a univariant system, then, just as water and water-vapor (i.e., $F=1+2-2=1$) and so in each we have a definite pressure for each temperature within certain limits. This formula for the degree of freedom is used as a system of classification for equilibria, and accordingly we have invariant, univariant, bivariant, multivariant systems, the members of each group behaving similarly.

30. Derivation of the phase rule.—Although this derivation is not the original one of Gibbs, it may serve to show how such a relation can be deduced without hypothesis and solely by mathematical reasoning.

Imagine an invariant equilibrium consisting of y phases of n components. Consider one phase alone. This phase will contain, then, a certain amount of all the n components. It may be a gas or a liquid, for all components go into the gaseous form and into solution at least to a slight extent.

In this phase which we are considering let the concentrations of the n components be $c_1c_2 \ldots c_n$. Since the equilibrium is invariant, the composition of this phase will be altered by a change of concentration, temperature, or pressure of the system. A change in one of these will cause a corresponding change in the other two. This we may express by the equation

$$f(c_1c_2 \ldots c_n, p, T)=0,$$

where f is any function of the variables.

The composition of one phase, however, determines that of all others which are in equilibrium with it; for all phases which are in equilibrium with one must be in equilibrium with each other, and this is only possible for a certain ratio of concentration between the constituents. Thus for a certain liquid phase we have a certain gaseous one in equilibrium with it and perhaps a solid. It follows, then, that the composition of all the phases is a certain function of the same variables. For each phase, then, we have an equation of the form

$$f(c_1 c_2 \ . \ . \ . \ c_n, p, T)=0.$$

Since there are y phases, we must have y equations of this form. There are, however, $n+2$ variables in each equation, so that if $y=n+2$, i.e., if we have two more phases than components, we may find a certain definite value for each unknown quantity, since we have the same number of equations as of unknown quantities. In this case there is *only one* value for each $c_1 c_2 \ . \ . \ . \ c_n$, p, and T at which the system may exist in equilibrium. *When n components are present in $n+2$ phases we have equilibrium only for a certain temperature, a certain pressure, and a certain ratio of concentration of the single phases, i.e., $n+2$ phases of n components can only exist at a certain point (transition point) in a system of coordinates.*

If one of these values is changed, then one phase disappears entirely, and we have $n+1$ phases of n components. In this case there will be $n+2$ variables (unknown quantities) in $n+1$ equations; hence it is not possible to find an absolute value for any one. We find, however, relative values of the $n+2$ variables $c_1c_2 \ldots c_n$, p, T, i.e., for each value of T we have only a certain value of p and of each of the terms $c_1c_2 \ldots c_n$ at which equilibrium can exist. *It is necessary to have at least n components present in order that a system containing $n+1$ phases may exist as a univariant equilibrium.*

Where we have $n+1$ phases of n components, and the conditions are altered, one phase disappears and we have n phases (equations) and $n+2$ variables (unknown quantities), i.e., the composition of the phases is uncertain and we have a divariant equilibrium. Such a one is a mixture of water and alcohol, i.e., two components in two phases, liquid and gas. At a low temperature we shall have a univariant equilibrium, for ice is formed and two components are present in three phases.

31. The equilibrium of water in its phases.—SOLID SOLUTIONS AND COMPOUNDS.—Fig. 5 gives the curves for water when plotted in a system of coordinates of which the abscissæ are temperatures and the ordinates are pressures—in other words, the pressure curves for water and ice, and the $p.t$ curve for water-vapor. Along the curve WV liquid and gas form a univariant equilibrium. The curve IV is made up of the values at which gas and solid can exist in univariant equilibrium, i.e., it is the vapor-pressure curve for ice. The curve *IW* represents the conditions for the coexistence of water and ice. As the freezing-point is but slightly influenced by pressure, this curve forms only a slight angle to the axis of pressures (1 atmos. = depression of 0.00752°).

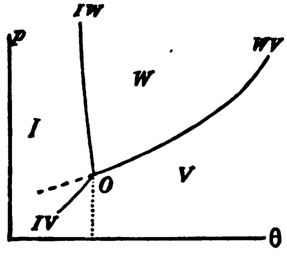

FIG. 5.

The point in which the three curves intersect is the ***transition-point***, i.e., the triple point in which all three phases can exist in equilibrium. This is at 0° the pressure being 4.6 mm. of Hg.

If we start with the system containing water and vapor (i.e., down the curve *WV*) in a closed vessel from which heat can be absorbed the point of intersection will be reached, part of the water will freeze, and we shall have three phases of one substance, i.e., the transition-point. If the temperature is still decreased either the liquid or the gaseous phase will disappear. Which of these depends upon the ratio of volume. If the volume of vapor is great enough, all the liquid will freeze and the curve *IV* will be followed. On the other hand, if the volume of liquid is large all gas will disappear and the curve *IW* will be produced, for the amount of ice which separates will increase the pressure and thus cause all the gas to condense.

In a system of coordinates, then, *a divariant equilibrium is represented by a surface, i.e., W, V, and I; a univariant equilibrium by a line, as WV, IW, and IV; and an invariant equilibrium by a point, as O.*

SOLID SOLUTIONS AND COMPOUNDS.—Assume we dissolve two salts, incapable of reacting, in an amount of water too small to completely dissolve either; ammonium chloride and ammonium nitrate, for example. We would have, then, three independent components and three phases (the two salts and the solution), i.e., a bivarient system and equilibrium can exist under any pressure at every temperature, when it is once established at a given temperature. And the solution saturated with each of the two salts should have a perfectly definite composition, independent of the amounts of the salts and of water.

Using potassium sulphate and ammonium sulphate, however, these relations are not observed; the composition of the solution at equilibrium depends upon the relative amounts of the two salts and water that have been mixed. The addition of one or the other of the two salts causes the solution to become enriched relatively in amount of the salt added, and poorer in the other salt. This is the behavior of a multivariant system, three components in two phases, i.e., the number of phases can only be two; the two isomorphous salts must form mixed crystals, or a *solid solution* and act together as a single phase.

Suppose ammonia gas is absorbed by a solid. Does the ammonia form with the solid a definite compound or a solid solution? If a compound is formed we must have three phases: ammonia gas, the solid, and the compound. The system would then be univariant, and for each temperature T there must be a definite dissociation pressure P. If ammonia gas is removed, more of the compound will dissociate and restore the value P. *A fixed dissociation pressure, then, characterizes the presence of a compound;* an example of this is ammonia with the solid metallic chlorides. If a solid solution of gas and solid had been formed the behavior would have been quite different. The system formed of two phases, ammonia gas and the solid solution, is bivariant; at a single temperature T the system will be in equilibrium for an infinite number of pressures of ammonia gas, will increase on addition of ammonia and decrease on the removal of ammonia. *The absence of a fixed dissociation pressure characterizes the pressure of a solid solution.* An example of this is ammonia gas and solid carbon.

32. The phase rule and the indentification of basic salts.—An exceedingly clever and most important application of the phase rule to inorganic chemistry has been made by Miller and Kenrick.* In the identification of basic salts we have a problem which up to the present has seemed utterly impossible of accurate solution. By the application by Miller and Kenrick of the phase rule, however, a great field is opened up and there seems to be no reason now why this subject should not be removed entirely from the position of mystery which it has occupied in the past. Naturally analysis alone cannot give much aid in an investigation, for by it it is not possible to tell whether a chemical individual is present or a mixture in varying amounts of two or more chemical individuals.

Applying the phase rule to the formation of basic salts by the action of water on chloride of antimony or on the nitrate of bismuth, the temperature being low and constant and the pressure being atmospheric, we know: (1) that if the system which consists of three components has arrived at equilibrium not more than three phases can coexist. Of these the solution forms one, and the precipitate must be either *one* single homogeneous substance (one phase), or a mixture of two *phases*, for instance, of two basic salts, or of one basic salt with the oxide. (2)

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* See Jour. Phys. Chem., 7, 259, 1903, of which I have made very free use.

That if the observed difference in composition between two precipitates by the action of different quantities of water on the same salt is due to their being mixtures of the same pair of basic salts in different proportions, the composition of the mother liquors will be the same in the two cases. (For the solution must be in equilibrium with both phases, whatever their actual amount.) The possible cases are thus divided into three groups:

1. The solutions are identical in composition in different experiments, while the composition of the precipitate varies.—The precipitate is a mixture of two phases.

2. The solutions differ in composition, but the precipitates have the same composition.—The precipitate is a single chemical compound.

3. Both solutions and precipitates vary.—The precipitate is a single phase of variable composition, a "solid solution."

If it were possible to represent the compositions of the solution by abscissæ, and those of the precipitates by ordinates, the results of a series of experiments could be represented by a curve; perpendicular lines would then correspond to case 1, horizontal lines to case 2, and slanting lines to case 3. In a three-component system this is not possible in general. In many cases, however, a pair or pairs of components may be found whose ratio in the solution or precipitate changes whenever the composition of the solution or precipitate changes, and only then; and since for the interpretation of the results it is only necessary to know whether the composition of solutions and precipitates remains constant or changes from experiment to experiment, it is sufficient to plot these ratios instead of the compositions themselves.

Since in the case of the action of water on nitrate of bismuth the precipitates are all of the general formula $m\mathrm{Bi_2O_3}$, $\mathrm{N_2O_5}$, $n\mathrm{H_2O}$, the compositions of the solutions, also, may be expressed in terms of $\mathrm{Bi_2O_3}$, $\mathrm{N_2O_5}$, and $\mathrm{H_2O}$, which are the components of the system. In the curve below the abscissæ give the ratios between $\mathrm{N_2O_5}$ and $\mathrm{H_2O}$ in the solutions, the ordinates those between $\mathrm{Bi_2O_3}$ and $\mathrm{N_2O_5}$ in the precipitates.* The only basic nitrates found are the two noticed in the curve and $\mathrm{Bi_2O_3 \cdot N_2O_5 \cdot 2H_2O}$, and all the others which have been supposed to exist were found to be mixtures of these in differing proportions. The vertical line corre-

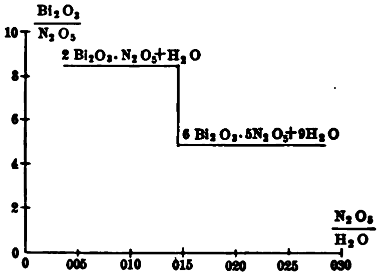

FIG. 6

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* See Allen, Am. Chem. Jour., 25, 307, 1901.

sponds to mixtures of precipitates, and the horizontal ones to pure chemical individuals.

In the same way Hawley (Jour. Phys. Chem., 10, 654–657, 1906) has proved that white lead is a compound of the composition $PbO_2H_2 \cdot 2PbCO_3$, and not a solid solution. Cox (Jour. Amer. Chem. Soc., 28, 1694–1710, 1906) has applied it to the chromates of mercury, bismuth, and lead; and Bell and Taber (J. Phys. Chem., 12, 171–179, 1908) to copper sulphate, showing that all basic sulphates of copper are simply solid solutions.

It will be seen from this brief sketch that the phase rule itself is not at all difficult to understand, but that its applications may give trouble, owing to the difficulty in choosing the components and other details. For further applications to metallurgy and to chemistry the reader must be referred elsewhere, for here it is only a question of the general principles involved in the law itself.

CHAPTER VI.

SOLUTIONS.

33. Definition of a solution.—*A solution is a hom*
geneous mixture which undergoes a change in compositio
in producing a new phase (see p. 117). In case the ne
phase has the same composition as the remainder th
substance is a *chemical individual* with reference to th
formation of that phase; but a change of conditions,
higher temperature and a lower pressure, will ofte
transform this into a mixture or a solution. Thus a 20
per cent solution of hydrochloric acid in water boil
under atmospheric pressure, at 110° and behaves like
chemical individual, i.e., gives off a vapor of the sa
composition as the liquid it leaves behind, but under
pressure of 2 atmospheres proves to be a solution, for t
vapor contains but 19 per cent of hydrochloric acid. A
water vapor, which at low temperature behaves as
chemical individual, proves to be a solution at a v
high temperature. When no possible change we h
brought about indicates the presence of a solution o
mixture, the substance is said to be a *chemical element*

The power to form solutions varies with the state of aggregation. Thus for gases it is unconditioned, while for solids, the opposite extreme, it is small, though still present.

34. Gases in liquids.—A true solution here is one in which there is no chemical reaction between the liquid and the gas, i.e., the gas may be expelled by heat. Henry's law, which was verified by Bunsen, enables us to find the amount of gas which will be absorbed. *When a gas is absorbed in a liquid the weight dissolved is proportional to the pressure of the gas.* Since, however, pressure and volume (at constant temperature) are inversely proportional, the law may also be expressed as follows: *A given amount of liquid absorbs at any pressure the same volume of gas.* If now we introduce the idea of concentration (the number of moles of substance divided by the volume). instead of the pressure, we obtain still another form for the law: *The amount of gas dissolved by a liquid is such that there is always a constant ratio between the concentration of the gas in the liquid and in the space above it.* This ratio does not depend upon the actual concentrations, being the same for all concentrations within wide limits, and its size is dependent only upon the nature of the liquid and its temperature.

If, instead of a single gas, a mixture of gases is dissolved, this law also holds, in that each constituent is absorbed from the mixture to the same extent as if it were present alone at a pressure equal to its partial pressure in the mixture.

Among the characteristics of a gas absorbed in a liquid are the following: There is less absorption in a solution than in a pure solvent, and addition of a substance to a liquid already containing gas forces this out. A liquid is easily supersaturated with gas, i.e., reduction of the pressure does not cause the gas to evolve immediately. The presence of dust or another gas, porous solids enclosing air and free from the gas in question, all cause the gas to be evolved.

When a gas is absorbed in a liquid there is always a change of volume in the latter. As a general rule the less compressible a gas is, the greater is the increase of volume caused by it. The increase of volume caused by the solution of a gas has been found to be approximately equal to the value *b* in the equations of Budde and Van der Waals (pp. 34, 35), as is shown for several gases in Table II.

TABLE II.

Gas.	Δv	b
O	0.00115	0.000890
N	0.00145	0.001359
H	0.00106	0.000887

35. Liquids in liquids.—We have in this case three possibilities:

1. No solubility, i.e., the formation of two layers and no homogeneous mixture.

. A mutual solubility, but not in all proportions (as er in ether = 3% and ether in water = 10%).

. The same relation as with gases, i.e., a solubility in proportions (as water and ethyl alcohol).

'he volume of liquid mixtures is not an additive pro- y. The volume is never equal to the sum of those ie constituents. Almost all mixtures possess a volume ller, but a few larger, than the sum of the partial imes.

'he most important point for us to consider here con- ing these mixtures is the manner in which they distil. shall consider first (1) cases where two completely niscible liquids are present; next (2) those which e a mutual solubility; and finally (3) those for which mixture is homogeneous.

· A liquid which consists of two immiscible constitu- , present in two layers, has a vapor-pressure equal to sum of those of the constituents. The boiling-point uch a system, then, is that temperature at which the or-pressure becomes equal to the pressure of the osphere; it lies still lower, therefore, than the boiling- it of the lower boiling constituent. This is difficult observe experimentally by direct heating, owing to bumping. If, however, the vapor of another boiling iid is passed through the mixture the whole is heated nly and to the same degree, and the mixture distils low the temperature at which either constituent alone will do so. An example of vapor pressure as an additive property is given by a mixture of water and carbon disulphide. At 26°.87 the vapor-pressure of water is 26.3 mm., that of carbon disulphide is 388.7, so that of the mixture should be 415.0, while experiment shows 412.3 mm.

Assume the vapor-pressures of the constituents to be p_1 and p_2; the volume of each in the vapor which distils over will be proportional to these pressures, and the total vapor-pressure will be equal to the sum of those of the constituents in the pure state. The weight of the vapor of each is equal to its density multiplied by its volume, or, by what is proportional to it, its vapor-pressure. We have, then, the weights (q_1 and q_2) of the constituents in the vapor from the proportion

$$q_1 : q_2 :: p_1 d_1 : p_2 d_2,$$

i.e., *the weight of a constituent distilling at any temperature from a system of two immiscible liquids is proportional to the product of the vapor-pressure of the pure constituent, at that temperature, and its density as a gas.*

2. In the case of a mixture of partially miscible liquids, i.e., where each is mutually soluble in the other, we have also a constant boiling-point and a constant distillate so long as two layers remain. The boiling-point here may be higher, equal to, or, as for class 1, lower than that of the lower boiling liquid. It cannot, how-

ever, be higher than that of the higher boiling constituent. With regard to the vapor-pressures of the two layers formed when the two constituents are to a slight degree mutually soluble, Konowalow has shown that *the liquid B when saturated with A has the same vapor-pressure as a liquid A when saturated with B, both being at the same temperature.* The composition of the liquid distilled is constant here, as is the temperature of boiling, so long as the two layers are present, independent of the amounts of the two constituents. When but one layer remains, its behavior is similar to the liquid in class 3.

3. When the liquids mix in all proportions, or in general when there is only one layer of liquid, it is possible to make a complete separation of the constituents by a fractional distillation, if the vapor-pressures of all mixtures lie between the vapor-pressures of the pure constituents, for then the lowest boiling distillate will be the pure constituent with the higher vapor-pressure.

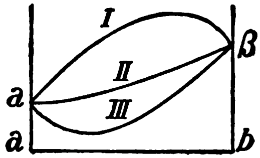

Fig. 7.

If we use a system of coordinates in which the vapor-pressures are laid out upon the axis of ordinates, and the percentage composition of the liquid upon the axis of abscissæ, we find that the vapor-pressure never reaches the sum of those of the constituents, but at times goes even below the smaller of these. Fig. 7 gives three types of curves thus obtained, which will illustrate the principle involved. We find in I a maxtmum of the vapor-pressure corresponding to a certain strength of solution. In II this maximum has disappeared, and the vapor-pressure of every mixture lies between those of the pure constituents, while in III the opposite extreme to I is observed, i.e., a minimum of the vapor-pressure which corresponds to a certain composition.

I. Mixtures which correspond to this type possess a maximum of the vapor-pressure for a certain composition, i.e., the lowest boiling liquid is a solution of a certain strength. An example of this is a 75% solution of propyl alcohol in water. This 75% solution will distil at the lower temperature from any propyl-alcohol solution until one of the constituents, i.e., either the water or the propyl alcohol, has disappeared, when the other will remain behind in the almost pure state. Thus if we start with a 50% solution of propyl alcohol a 75% solution will be distilled until all the alcohol is removed and water is left in the flask. If we start with a 90% solution of the alcohol the 75% solution will be given off until all the water has been used up and pure propyl alcohol remains behind.

II. For mixtures of this type we can make a complete separation by distillation. The vapor pressure of all mixtures lies between those of the two constituents; consequently the one with the higher vapor-pressure will be given off in the almost pure state, leaving the other behind. A solution of benzol in *m*-xylol belongs to this class. The method of calculating the value of the vapor- pressure in such a case will be given later.

III. Here we have a minimum of the vapor-pressure corresponding to a certain composition. A solution of this composition will, then, always be the last to be distilled, since its boiling-point is the highest of all possible mixtures. This is just the opposite of case I, where the solution of a certain composition is given off first. All solutions, for example, of formic acid and water will distil off an amount of one constituent until the solution remaining contains 70% of formic acid. A 90% solution will give off almost pure formic acid until just enough remains to form a 70% solution. A 50% solution will give off water until the 70% solution is left behind.

It will be observed here that in cases I and III we find systems which behave as chemical individuals, or compounds (p. 130), i.e., the 75% solution of propyl alcohol in water, and the one containing 70% of formic acid. That these simply appear as chemical individuals only under this one condition is proven by the fact that the composition of the vapor phase varies with the pressure under which the distillation takes place.

An interesting technical application of these principles and facts has been made by Young (Trans. Chem. Soc., 81, 707, 1902) in his method of preparing absolute alcohol from strong spirit. As is well known ethyl alcohol and water form a constant boiling liquid (B.P. = 78°.15) of a composition of 95.57% of alcohol and 4.43% of water, which by distillation alone cannot be further separated. Instead of employing a dehydrating agent and distilling the alcohol alone, as has been the common practice, he mixes with the solution benzene, *n*-hexane, or a similar liquid. The behavior of this system on distilling can be seen from the table below:

Liquid of Cconstant B.P.	B.P.	Percentage Composition.		
		Alcohol.	Water.	Benzene.
1. Alcohol, water and benzene...	64°.85	18.5	7.4	74.1
2. Alcohol and benzene........	68°.25	32.41	......	67.59
3. Water and benzene..........	69°.25	......	8.83	91.17
4. Alcohol and water...........	78°.15	95.57	4.43	......
5. Alcohol....................	78°.3	100.0	......	......
6. Benzene....................	80°.2	......	......	100
7. Water......................	100°.0	......	100	......

The lowest boiling-liquid is the ternary system W.A.B. and, unless one liquid is present in a relatively ver small quantity, it will distil first. If there is more than sufficient benzene to carry over the whole of the water, and if alcohol is present in excess, the ternary mixture will be followed by the binary mixture (A.B.), and the last substance to come over will be alcohol. Owing to the fact that there is but 3°.4 difference between the boiling-points of the ternary mixture (A.B.W.) and the binary one (A.B.), however, it is impossible to get rid of all the water in one distillation. By redistilling the partially dehydrated alcohol once or twice with a further quantity of benzene complete separation is effected. As the alcohol itself need not be distilled, but can be poured directly from the still, and as the benzene can be recovered without difficulty, this method has many advantages.

36. Solids in liquids.—When a soluble solid comes in contact with a liquid it dissolves. When no more substance is taken up by the liquid at any one temperature the solution is said to be saturated at that temperature. There are two general methods of making a saturated solution; but in either it is always to be remembered that *in order that a solution be saturated the solid substance must be in contact with it.*

I. The substance, in granular form, is brought into the liquid, and the system agitated at a certain temperature until no more is dissolved; or,

II. The solution is made as above, but at a higher temperature than the desired one, to which it is reduced later.

Both these methods give the same result if properly carried out, although the latter is quicker and so to be preferred.

The importance of the state of the solid from which the solution is made has recently been pointed out by Hulett (J. Am. Chem. Soc., 27, 49, 1905). I quote from him: "The explanation of the phenomenon" (of the greater speed of solution and greater solubility of very small particles of solid) "is based on the following considerations: The boundary between a solid and a liquid is the seat of a certain amount of energy due to the surface-energy of the liquid; if this surface is increased by powdering the solid, the total surface-energy is correspondingly increased. Further, it is a generally observed fact that the form of a substance which has the greater free energy is the more soluble, has the greater vapor-pressure, and is the least stable form, e.g., allotropic modifications of substances have different solubilities, and the unstable form is always the more soluble. This phenomenon is hardly analogous to the well-known behavior of liquid drops of different sizes. Small drops in the vicinity of large ones grow small and disappear, while the larger ones grow larger, and the reason is quite clear. It is known that the curved surface of a liquid greater vapor-pressure than a plane or less curved , therefore, a distillation takes place. The ity between the vapor-pressure of liquids and the 1-pressure of solids has suggested to some the between the facts just mentioned and the be- of solid particles of different sizes in contact with ution. But we cannot assume that the surfaces of ticles of a powder are curved, or, if that is granted, not know that a curved surface of a solid or a dge has a greater solution-pressure than a plane of the same substance."

tt has found that a solution of gypsum saturated containing 2.080 grs. $CaSO_4$ per liter (i.e., 0.01530 vill increase its concentration rapidly to a maximum naken with powdered gypsum and then will decrease original value again. In one experiment the con- gypsum reached 2.542 grs. $CaSO_4$ in a liter in a The fine powder used for this purpose was after the concentration had reached its original o have increased in the size of its grain. The t particles thus go into solution, produce the turation and are then deposited upon the others, all increase in size.

s been observed that crystals dissolve more rapidly directions than in others, and it is possible thus to a circular disk of gypsum (cut parallel to 010) me elliptical by the action of dilute hydrochloric acid. Hulett calls attention, however, to the fact that solubility has nothing to do with rate of solubility, *for solubility is measured by the concentration of the solution which is in final equilibrium with the solid.* He found that the plate of gypsum is equally soluble in all directions, and a solution saturated with planes cut in one direction is in equilibrium with those cut in other directions. For these reasons Hulett advocates the preparation of saturated solutions from large particles, as there is then no danger of supersaturation, and the liquid need not be filtered. In case small particles are used and a supersaturation feared, contact with the large particles or crystals will cause the equilibrium to be attained from the *supersaturated* side.

It is often possible to cool a saturated solution (which has been separated from its solid phase) to such an extent that it is supersaturated. Some solutions of this sort can be kept indefinitely, provided germs of the solid phase are excluded. Such solutions are called *metastable.* On the other hand, there are some solutions in which the solid phase appears even when its germs are excluded. Such solutions are called *labile.* The distinction between these two kinds of solution is not so sharp as one would think, however, for by overcooling sufficiently the metastable solution may pass over into the labile state. In general the metastable solution is smaller in concentration than is that which is labile. Increase of the concentration causes the metastable state to be transformed into the labile; the concentration at which this occurs is called the *metastable limit.*

37. Osmotic pressure.—If in a tall jar we place a layer of pure water over a colored solution we observe after a time that the whole liquid is colored. The colored substance has diffused through the liquid until a homogeneous mixture results. This action shows that there must be a certain tendency or pressure which causes the substance to occupy the entire space available. This pressure causing the substance to diffuse into the solvent is called *the osmotic pressure of that solution.* If a vessel is provided with a partition of such a nature that it allows free passage to the solvent, but not to the solute, and we have water on one side and a solution on the other, the solute will exert a pressure upon it; this is the osmotic pressure of that solution. Semipermeable partitions of this sort had been found by Traube, and perfected by Pfeffer and Morse and his co-workers in such a way that it is now possible to actually measure the different osmotic pressures by means of a manometer. An apparatus by which the principle of Pfeffer's measurements may be understood is shown in Fig. 8. The cylinder *A* is made of porous clay, and is designed to support the semipermeable film. To produce this the pores of the cylinder are filled with a solution of copper sulphate. After the excess of this is removed the cup is filled with a 3% solution of potassium ferrocyanide, and allowed to stand for a day in a solution of copper sulphate. In this way the pores are filled with a film of copper ferrocyanide, which is permeable to water, but not to a large number of salts. The process of measuring is as follows: The now semipermeable cylinder is washed out and filled with the solution to be measured. The rubber stopper *CC* is next inserted in *A* in such a way that the solution rises a short distance in the tube, i.e., the cylinder is entirely filled with solution without air, and the tube connected to a manometer. The cork *BB* is then fastened in the vessel *DD*, which is filled with water. The liquid rises slowly in the tube until equilibrium is reached, i.e., until the resistance in the manometer is just equal to the osmotic pressure. The height of the column of mercury thus represents the osmotic pressure of the solution in *A*.

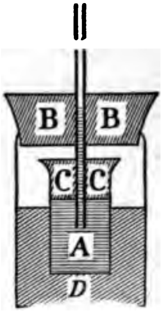

FIG. 8.

There is a definite attraction, then, or an apparent one, between the substance in solution and the solvent, and this is of such a nature that without the partition it would cause the system to become homogeneous. Whether this apparent attraction is actually an attraction between solvent and solute, or whether it is a tendency for the solute to become uniform in concentration in the liquid, owing to forces existing in it, is unknown. As under certain conditions a change in the solvent makes no difference in the osmotic pressure observed (and when it does it can be accounted for quite readily) it would seem that the latter supposition is the more correct.

However, whether this phenomenon is a pressure or an attraction can have no difference from our standpoint, for what we shall designate as osmotic pressure is an experimentally observed fact which has been given that name. *As such, then, we can define osmotic pressure* (as we shall use the term) *as that pressure which will just prevent pure solvent from going through a semipermeable partition to dilute the solution contained within it.*

The nature of the semipermeable partition seems to have no effect upon the value of the osmotic pressure. That this must be true can be proven by the following process: Imagine A and B (Fig. 9) to be two unlike semipermeable partitions placed in a cylinder of glass. Assume the cylinder full of solution and lowered in a horizontal position in a vessel of water. If the pressure P is exerted by the partition A, and p

(a smaller one) by B, then water will go through A until the internal pressure P is reached. Since B allows only the pressure p, however, this pressure P can never be reached, so that we would have a steady current of water going from A to B under the finite pressure $P-p$. This, however, would be a perpetual motion, which is impossible; hence the partition A must give rise to the same osmotic pressure as the partition B.

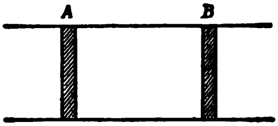

FIG. 9.

Osmotic pressure is, then, independent of the nature of the solvent and the partition, the latter being simply a means of making it visible.

Pfeffer measured, by means of an apparatus of the type of the one described, the osmotic pressures which exist in a large number of solutions and found them in many cases to be very great. A few results for sugar solutions of varying concentrations at 15° C. are given in Table III.

TABLE III.

c	p	p/c	c	p	p/c
1	53.8	53.8	4	208.2	52.1
1	53.2	53.2	6	307.5	51.3
2	101.6	50.8	1	53.5	53.5
2.74	151.8	55.4			

here c is the percentage composition of the solution is the osmotic pressure, in cms. of mercury, and p/c the ratio of pressure to concentration.

Considering the difficulties in measuring and the perfections in the semipermeable film, the term p/c to be considered as constant; hence *the osmotic presure is proportional to the concentration of the solute.* urther results at different temperatures showed that *e osmotic pressure is proportional to the absolute temerature.* This, however, is only strictly true when the eat of dilution of the solution is zero, i.e., when the soluon is dilute. On account of experimental difficulties e direct effect of this heat of dilution upon the osmotic ressure of concentrated solutions has not as yet been etermined.

van't Hoff in 1887 from this much knowledge derived, y the aid of thermodynamics, an analogy between the ehavior of gases and substances in solution. Here, however, we shall not go into his reasoning, but shall consider how his results may be arrived at in a more simple manner.

As we have seen by Pfeffer's results, the term p/c remains constant for any one solution when p is the osmotic pressure and c the concentration. $1/c$, however, is equal to v, the volume; we have then

$$p/c = pv.$$

Since now the osmotic pressure is proportional to the absolute temperature, as is also the term p/c, we have

$$pv = \text{constant} \times T.$$

This equation is so much like the one for gases (1) that it immediately suggests that there is some kind of a connection between them and substances in solution. If now the value of the constant is determined, then by comparing it with the gas constant it is possible to find this connection. Since we are to use the molecular gas constant in the comparison, it will be necessary also to find this constant for 1 mole. A 1% solution of sugar at 0° is held in equilibrium by a column of mercury 49.3 cms. high and thus gives an osmotic pressure equal to

$$49.3 \times 13.59 = 671 \text{ grams per sq. cm.}$$

Since the molecular weight of sugar ($C_{11}H_{22}O_{11}$) is 342, the volume in which 1 mole is dissolved (to give a 1% solution) is 34200 cc. We have then

$$\text{constant} = \frac{p_0 V_0}{T} = \frac{671 \times 34200}{273} = 84200 \text{ gr.-cms.,}$$

while the molecular gas constant is

$$R = 84800 \text{ gr.-cms.}$$

The constant is the same, then (within the experimental error), for the gaseous state and the state of a substance in solution; consequently for each state, considering 1 mole, we have

$$pV = RT.$$

van't Hoff summed up these results in the following form: *The osmotic pressure of a substance in solution is the same pressure which that substance would exert were it in gaseous form at the same temperature and occupying the same volume.*

Since 1 mole of gas at 0° and 76 cms. of Hg occupies the volume of 22.4 liters, at the volume of 1 liter it will have, *according to van't Hoff's law,* the pressure of 22.4 atmospheres (Boyle's law). This pressure, 22.4 atmospheres, is then the osmotic pressure which is exerted by 1 mole of solute in 1 liter of solution at 0°, i.e., by a molar solution. From this osmotic pressure, 22.4 atmospheres, it is very easy to find that for any other concentration given in terms normal. Thus a $n/10$ solution gives an osmotic pressure of 2.24 atmospheres.

Morse and Frazer (Am. Chem. J., 34, 1, 1905; 37, 324, 425, 558; 38, 175, 1907), in an apparatus similar to that of Pfeffer, but greatly refined, have measured osmotic pressures of sugar and glucose solutions up to 25 atmospheres. Their results for strong solutions of sugar at 20° show that van't Hoff's law holds, *provided* *the volume of pure solvent is substituted in the law that of the solution.* In place of the above law

$$p=\frac{RT}{V},$$

where V is the volume of the solution, they find

$$p=\frac{RT}{V'},$$

where V' is *the volume of the pure solvent,* corresponds more closely with their experimental results.

Morse and Frazer sum up their results as follows: "*When we dissolved a gram-molecular weight of cane sugar* (342.22 *grams*) *in* 1000 *grams of water, i.e., in the mass of solvent which has the unit volume,* 1 *liter, at the temperature of maximum density—we found its osmotic pressure, at about* 20°, *in quite close accord with the pressure which a gram-molecular weight of hydrogen would exert, at the same temperature, if its volume were reduced to* 1 *liter, i.e., to that volume which the unit mass of solvent has at the temperature of greatest density.*"

For cane-sugar, then, and presumably for all other substances, we can express the law as follows: *A substance in solution* "*exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state.*" Or, in other words, it "*exerts an osmotic pressure throughout the larger volume of the solution equal to that which as a gas it would exert if confined to the smaller volume of the pure solvent.*"

This law of van't Hoff's, as modified by Morse and his co-workers, enables us now to define the molecular weight of a dissolved substance, and the definition naturally reminds one of the definition for substances in the gaseous state. *The molecular weight of a substance in solution is the weight in grams which in the volume of approximately* 22.4 *liters of solvent will give an osmotic pressure of* 1 *atmosphere at* 0° *C., or a corresponding value at another temperature or volume.*

If the osmotic pressure of a solution is known it is then possible to find from it the molecular weight. A 2% solution of sugar gives, at 0° C., an osmotic pressure equal to 101.6 cms. of Hg. If this solution contained 1 mole in 1000 grams of water it would give a pressure equal to $22.4 \times 76 = 1702.4$ cms. of Hg. The 2% solution contains 20 grams to the liter; hence $20 : M :: 101.6 : 1702.4$; $M = 335$.

Results for sugar and glucose obtained by Morse and his co-workers are summarized in the following tables, and will serve to show the agreement between the determined and calculated values. It is to be remembered here that the diulte solutions are more affected by the experimental and unavoidable error than the others, so that the apparently abnormal figures for the 0.1 solution may be disregarded. The molecular wei is calculated from the proportion

$$M : 22.265\frac{273+t}{273} :: w : P,$$

where 22.265 is the volume of 2 grams (not hydrogen at Baltimore, M is the molecular w substance dissolved in 1 liter of water, and observed osmotic pressure at the temperature t grams of the substance are dissolved in 1 liter of

Osmotic Pressures of Cane-sugar.

Weight normal concentration.	Temperature of solution.	Observed osmotic pressure. Atmospheres.	Theoretical gas pressure at same temperature. Atmospheres.	Difference between osmotic and gas pressure.	Molecular weight calculated from osmotic pressure.
0.1	24°.06	2.51	2.42	+0.09	327.85
0.1	24°.23	2.55	2.43	+0.12	322.56
0.2	20°.90	4.72	4.79	−0.07	344.96
0.2	21°.38	4.78	4.80	−0.02	344.90
0.2	21°.77	4.81	4.81	0.00	339.74
0.3	21°.67	7.24	7.21	+0.03	338.37
0.3	19°.88	7.20	7.16	+0.04	338.20
0.4	21°.63	9.64	9.61	+0.03	338.73
0.4	22°.15	9.69	9.63	+0.06	337.50
0.5	22°.62	12.06	12.06	0.00	339.59
0.5	23°.70	12.23	12.10	+0.13	336.19
0.6	24°.38	14.74	14.55	+0.19	335.32
0.6	24°.24	14.70	14.55	+0.15	336.07
0.6	24°.10	14.77	14.54	+0.23	334.32
0.7	23°.64	16.95	16.94	+0.01	339.39
0.7	23°.90	16.96	16.93	+0.03	339.50
0.8	23°.60	19.30	19.35	−0.05	340.48
0.8	23°.69	19.39	19.36	+0.03	339.08
0.9	24°.79	21.82	21.86	−0.04	340.19
0.9	24°.76	21.91	21.86	+0.05	338.82
1.0	23°.56	24.42	24.19	+0.23	336.39
1.0	24°.58	23.98	24.28	−0.30	342.72

H = 1

Final mean of mol. weight, 33
Theoretical mol. weights, 33

Osmotic Pressures of Glucose.

Weight normal concentration.	Temperature of solution.	Observed osmotic pressure. Atmospheres.	Theoretical gas pressure at same temperature. Atmospheres.	Difference between osmotic and gas pressure.	Molecular weight calculated from osmotic pressure.	Mean molecular weight for each concentration.
0-1	24°.10	2.39	2.42	−0.03	181.40	180.62
0-1	25°.10	2.42	2.43	−0.01	179.83	
0-2	24°.10	4.76	4.85	−0.09	181.77	181.94
0-2	24°.93	4.77	4.86	−0.09	182.10	
0-3	22°.20	7.12	7.22	−0.10	181.38	181.06
0-3	23°.48	7.17	7.25	−0.08	180.73	
0-4	26°.90	9.70	9.78	−0.08	180.21	180.62
0-4	26°.60	9.65	9.77	−0.12	181.02	
0-5	21°.86	12.07	12.03	+0.04	178.12	179.35
0-5	24°.17	12.00	12.12	−0.12	180.57	
0-6	22°.57	14.56	14.46	+0.10	177.62	179.62
0-6	22°.40	14.32	14.40	−0.08	180.42	
0-6	22°.30	14.29	14.45	−0.16	180.83	
0-7	22°.26	16.82	16.85	−0.03	179.18	179.63
0-7	25°.43	16.96	17.04	−0.08	179.55	
0-7	22°.70	16.75	16.88	−0.13	180.16	
0-8	23°.00	19.27	19.31	−0.04	179.16	179.76
0-8	23°.28	19.16	19.33	−0.17	180.39	
0-8	23°.64	19.25	19.35	−0.10	179.73	
0-9	23°.80	21.64	21.80	−0.16	179.87	179.99
0-9	22°.58	21.49	21.70	−0.21	180.49	
0-9	23°.10	21.63	21.74	−0.11	179.60	
1-0	22°.20	24.12	24.08	+0.04	178.46	179.04
1-0	22°.60	24.00	24.11	−0.11	179.60	
1-0	22°.10	24.03	24.07	−0.04	179.07	

H=1 Mol. Wt. glucose=178.74 Mean mol. wt., 180.08

Lewis (Jour. Am. Chem. Soc., 30, 668–683, 1908) in a theoretical paper has called attention to the fact that the modified form of van't Hoff's equation, presented by Morse and Frazer, as epitomizing their results, is not satisfactory at higher concentrations, and advocates the equation (see also later),

$$P-\tfrac{1}{2}\alpha P^2=-\frac{RT}{V_0}\log_e N,$$

where α is the compressibility of the solvent, V_0 its molecular volume (volume of 1 mole), and N is the molar fraction of the solvent, i.e., moles of solvent divided by moles of solute plus moles of solvent.*

Lewis also calls attention to the fact that the osmotic pressure at one temperature may be found from that at another if the heat of dilution of the solution is known, and attributes the equality in osmotic pressure, at 0° and 20°, of sugar solutions, as found by Morse and Frazer, to the decreasing, and possibly negative, temperature coefficient of osmotic pressure.

Measurements of the osmotic pressures of strong solutions of sugar, galactose, massuite, and dextrose, have also been made by Berkeley and Hartley (Proc. Roy. Soc., 73, 433, 1904; Trans. Roy. Soc., 206, 481, 1906). It is not only water solutions that have been measured, however, for Raoult (Zeit. f. phys. Chem. 27, 737, 1895) has found that vulcanite allows passage to ether but not to methyl alcohol. Thus with ether on one side and an equal volume mixture of ether and methyl alcohol on the other, he observed an omotic pressure of 50 atmospheres at 13° C., when the manometer was fractured. In this case the pressure, just as with water solutions, was exerted in the solution, i.e., the pure solvent goes toward the solution and a pressure is necessary to prevent it.

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* 1 mole in a liter of water (i.e., $\frac{1000}{18}=55.5$ moles) gives a value of N equal to $\frac{55.5}{55.5+1}=0.982+$.

There is one characteristic of osmotic phenomena which must be mentioned. It is the slow rise of the pressure up to its maximum value. Thus with a half-molar sugar solution Morse and Frazer found 95 hours necessary for the establishment of the final equilibrium. This, naturally, is to be attributed to the resistance of the cell to diffusion.

A simple and quick method of observing the effect of osmotic pressure is given by Tammann. If in a moderately strong solution of copper sulphate we place a drop of a strong solution of potassium ferrocyanide it is immediately surrounded by a semipermeable film of copper ferrocyanide. Since the ferrocyanide solution is more concentrated than that of the copper sulphate, water goes through the film, from the copper salt to the ferrocyanide, and dark streaks are observed to sink from the bubble. These streaks are of stronger copper-sulphate solution, which is formed from the other by the loss of water, and sink on account of their increased specific gravity. If the ferrocyanide solution is weak and another salt or more ferrocyanide is added to it until no streaks are observed to sink from a bubble, then there must be an equal number of moles per liter in both of the two sol tions, i.e., in the copper solution and the ferrocyani plus salt. If the ferrocyanide solution is weaker th the one of copper sulphate (in moles per liter), then wat will go out of the bubble, which will decrease in si and light streaks will appear in the copper solution.

In this experiment the tendency for the solutions become of the same molar concentration is particular striking, and water is always observed to go from t more dilute to the more concentrated, expressed moles per liter.

Consider a cylinder, as shown in Fig. 10, filled wi a solution, and provided with a semipermeable pist *a*. If by a certain weight this piston is lowered, wat will go through it, and we shall have separated an amou

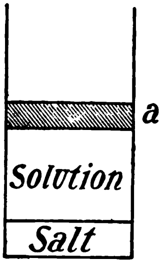

Fig. 10.

of solvent from the solution. If the amount of wat separated previously contained 1 mole of solute, and t total volume is very large, the osmotic work is given by the equation

$$pV=RT,$$

where V is the decrease in volume occupied by the solute under the constant osmotic pressure p. It is possible thus to determine the molecular weight of any substance in solution by finding the work necessary for the separation of a certain amount of the solvent. For each amount of solvent which has previously contained one mole of solute the work is (just as for gases) $2T$ cals, so that the number of moles in the definite amount of solvent removed may be calculated from the work, and from this the molecular weight of the solute can be found. *The molecular weight of a substance in solution by this method would be the weight which removed from a solution against its osmotic pressure would require the work of 2T cals.; or what is the same thing, the weight which has been dissolved in the volume of solvent requiring the work 2T cals. to remove reversibly from the main portion of the solution.*

38. Solution pressure.—The pressure which a solid exerts in going into solution is called the *solution pressure*. This term, naturally, is expressive of the fact that when the substance has dissolved it exerts osmotic pressure. Since the osmotic pressure increases with the amount of substance dissolved, the solution pressure of a substance can be no greater than its osmotic pressure in a saturated solution, for that pressure prevents the substance from dissolving further. A substance is less soluble in its own solution than in pure water, and it seems that it is the osmotic pressure which is due to that substance which effects its solubility principally; at any rate, no general law is known which governs the solubility of a substance in solutions of other substance, i.e., when the solution pressure is counteracted by an osmotic pressure due to another substance. The behavior of a substance dissolving, then, is very similar to a substance going into the gaseous state, and we have a solution pressure corresponding to the vapor-pressure.

39. Vapor-pressures of solutions.—It has been known for many years that the vapor-pressure of a solution is lower than that of the pure solvent. Babo (1848) and Wüllner (1856) found, further, that *the depression of the vapor-pressure is proportional to the amount of solute present; and for the same solution the depression for any temperature is the same fraction of the vapor-pressure of the pure solvent.*

If p is the vapor-pressure of the pure solvent, p' that of the solution, and w the percentage of solute, then

$$\frac{p-p'}{p}=kw,$$

where k is the relative depression, $\frac{p-p'}{p}$, for a 1% solution.

Raoult in 1887 found that a more general relation is obtained if the relative depression is determined for 1 mole of substance in a certain amount of solvent. By experiment he found that all solutions containing one mole of substance in a certain weight of solvent possesses the same vapor-pressure; i.e., *the* MOLECULAR *depression of the vapor-pressure is constant for all substances in the same solvent.* Further, he found that solutions of equimolecular amounts of substance in equal weights of different solvents give relative depressions of the vapor-pressure which are proportional to the molecular weights of the solvents. This shows that the vapor-pressure depends upon the relative number of moles of the solute and solvent.

Raoult summed up his results as follows: *One mole of any substance dissolved in 100 moles of any solvent causes a 1% depression of the vapor-pressure.* (Here the number of moles of solvent is calculated from the gaseous molecular weight.)

This law may also be expressed in another form: *The vapor-pressure of a solution is to that of the pure solvent as the number of moles of the solvent is to the total number of moles present in the solution, i.e. ,of solvent plus solute.*

For very dilute solutions the number of moles of the solute is so small in comparison with that of the solvent that the ratio becomes one, i.e., the vapor-pressure of the solution is practically the same as that of the solvent.

Some of Raoult's results for ethereal solutions (Zeit. f. phys. Chem., 2, 353–373, 1888) are given below, and will serve to show the truth of his two simple laws governing the vapor-pressure of a solution:

Substance in ether.	Moles of dissolved substance per 100 moles of solution.	$\frac{p-p'}{p}$ for solution.	$\frac{p-p'}{p}$ for a 1 mol per cent solution.
Turpentine...........	8.95	0.0885	0.0099
Methyl salicylic acid...	2.91	0.026	0.0089
Methyl benzoic acid...	9.60	0.091	0.0095
Benzoic acid..........	7.175	0.070	0.0097
Trichloracetic acid....	11.41	0.120	0.0105
Capryl alcohol........	6.27	0.070	0.0110
Aniline..............	7.66	0.081	0.0106

Substance in ether.	Moles of dissolved substance per 100 moles of solution.	$\frac{p'}{p}$	
		Observed.	Calculated.
Turpentine...........	5.9	0.94	0.941
"	12.1	0.881	0.879
Nitrobenzene.........	6.	0.945	0.940
Aniline..............	3.85	0.96	0.961
"	7.7	0.923	0.923
Ethyl benzoic acid....	4.9	0.949	0.951
"	9.6	0.909	0.904

We thus obtain another definition of the molecular weight of a substance in solution, and this as far as we know agrees perfectly, for dilute and moderately concentrated solutions, with our previous one based upon osmotic pressure. According to it *the molecular weight of a substance in solution is that weight which in* 100 *formula weights of the solvent depresses the vapor-pressure of this one hundredth of its value.*

Expressing the above laws as equations we obtain

$$\frac{p'}{p}=\frac{N}{N+n},$$

$$\frac{p-p'}{p}=\frac{n}{N+n},$$

where N is the number of moles of the solvent and n is the number of moles of the solute.

These equations will only hold when the solute is non-volatile, a condition which is practically fulfilled when its boiling-point is 140° above that of the solvent, and when n represents the correct number of moles in solution. The value of N here is the number of formula weights of solvent, i.e., the weight in grams divided by the molecular weight of *the solvent in the gaseous state;* n of course being the weight of solute (in the solvent) divided by its molecular weight *in the solution.*

For the direct determination of the molecular weight it is more convenient to use an altered and easily d rivable form of these equations, i.e.,

$$\frac{p-p'}{p'}=\frac{n}{N};$$

according to which *the depression of the vapor-pressu is to the vapor-pressure of the solution as the number moles of solute is to the number of moles of solvent.*

Since $n=\frac{w}{m}$, where w is the weight of solute and its molecular weight in the solution, and $N=\frac{W}{M}$, M r ferring to *the solvent as a gas*, we have

$$\frac{p-p'}{p'}=\frac{wM}{mW}, \quad \text{or} \quad m=\frac{wM}{W}\cdot\frac{p'}{p-p'}.$$

Example.—A solution of 2.47 grams of ethyl ber zoate in 100 grams of benzene has a vapor-pressure c 742.6 mm. of Hg, while pure benzene has one c 751.86 mm., both at 80° C. Find the molecular weig of ethyl benzoate. $w=2.47$, $M=78$, $W=10$ $p'=742.6$, $p=751.86$, $p-p'=9.26$; hence $m=154$ while from the chemical formula we find $C_6H_5COOC_2H$ $=150$.

Biddle (Am. Chem. J., 29, 341, 1903) gives a di ferential method for determining the difference in vapo pressures of pure solvent and solution (i.e., $p-p'$) fo any concentration and suggests calculating this to mole of substance in 100 grams of solvent, and using it as the molecular depression of the vapor-pressure. In this way, of course, it is possible to determine molecular weights of other substances *in that solvent* by the use of a simple proportion. Thus we would find $(p-p')$ for 1 mole$:(p-p')$ found$::1:x$, and x would represent the number of moles, i.e., $\frac{w}{m}$, contained in 100 grams of the solvent. Knowing the weight w, it is then easy to calculate m, the molecular weight.

Lewis (J. Am. Chem. Soc., 30, 668–683, 1908) calls attention to the fact that these laws of Raoult (with another mentioned later) are probably the most accurate we have for the behavior of substances in solution, for the van't Hoff osmotic pressure law gives absurdly low results for very high concentrations, and the Morse and Frazer modification gives abnormally high values at very high concentrations. In fact, according to Lewis, osmotic pressures at very high concentrations can be more accurately determined indirectly from the vapor-pressure than is possible by direct measurement. For this purpose he derives the equation

$$P-\tfrac{1}{2}\alpha P^2=\frac{RT}{V_0}\log_e\frac{p}{p'},$$

in which P is the osmotic pressure, α the coefficient of compressibility of the solvent, V_0 its molecular volume

(volume of 1 mole), and p and p' are respectively the vapor-pressure of pure solvent and solution.

In case it is desired to find the osmotic pressure at a temperature other than that at which p and p' are measured, use must be made of the equation $P-q=T\frac{dP}{dT}$, where q is the heat of dilution, i.e., the heat evolved when 1 cc. of solvent is added to a large quantity of the solution.

When both solvent and solute are volatile it is still possible to calculate the vapor-pressure of the mixture under certain conditions. The conditions here are these: That no chemical reaction takes place between the solvent and solute, and that the molecular weight in the liquid state is the same as that in the gaseous state, for both solvent and solute.

Since in such a case the vapor-pressure of each is depressed by the other we can find the total vapor-pressure by subtracting from the sum of the vapor-pressures (i.e., assuming that neither affects the other) the sum of the effects of each on the other. We have then

$$\pi=p_1+p_2-\left(p_1\frac{n_2}{n_1+n_2}+p_2\frac{n_1}{n_1+n_2}\right),$$

where the sub-numerals distinguish the two constituents the expressions $\frac{n_2}{n_1+n_2}$ and $\frac{n_1}{n_1+n_2}$ represent the *mole fraction* of each in the mixture, and the terms with parenthesis are obtained from the second of the equa- s above, considering each liquid in turn as the solvent. rearrangement this formula becomes

$$\pi = p_1\frac{n_1}{n_1+n_2} + p_2\frac{n_2}{n_1+n_2},$$

re the two terms represent the partial pressures of constituents *in the mixture*, or,

$$\pi = p_1' + p_2',$$

and p_2' being the partial pressures of each in the ture $\left(\text{i.e., } p_1\frac{n_1}{n_1+n_2} \text{ and } p_2\frac{n_2}{n_1+n_2}\right)$, p_1 and p_2 having resented the vapor-pressures at that temperature of pure substances as measured alone.

ince by Dalton's law the total pressure is equal to sum of the partial pressures, and these by definition gadro's law) are dependent upon the number of s in the gaseous space, we have (see p. 30)

$$\frac{p_1'}{\pi} = \frac{n_1'}{n_1'+n_2'} \quad \text{and} \quad \frac{p_2'}{\pi} = \frac{n_2'}{n_1'+n_2'}.$$

above equations only hold strictly for solutions of which act normally. In case they do not behave ly, by an appropriate change in the formula, their or may be expressed with some accuracy. Since ange gives no general relation for all substances, but necessitates the knowledge of specific constants for each we shall not consider it here.

For further information on this subject, see Zawidski, Zeit. f. phys. Chem., 35, 129, 1900; Gerber, Dissertation, Jena, 1904; Marshall, Trans. Chem. Soc., 89, 1351, 1906; Latty, *ibid.*, 92, 1957, 1907; and Bose, Phys. Zeit., 8, 353, 1907.

An example of the application of these relations is given by a mixture of benzene and ethylene chloride at 49°.99 C. The sub-numeral 1 refers throughout to the benzene.

29.79 moles of ethylene chloride, of which the vapor-pressure (p_2) is 236.2 mm. are mixed with 70.21 of benzene, $p_1 = 268$ mm. What is the total vapor-pressure of the mixture? We find

$$\pi = 268 \times 0.7021 + 236.2 \times 0.2979 = 258.42,$$

the observed value being 259 mm.

The molar fraction (i.e., moles of each to total moles) of each liquid in the gases distilling, then, is readily found by dividing the pressure of the constituent in the vapor by the total pressure, these being proportional to the moles of constituent in the vapor to the total moles. We have then

$$\frac{268 \times 0.7021}{258.42} = 0.728$$

and

$$\frac{236.2 \times 0.2979}{258.4} = 0.272,$$

.e., the distillate from the solution containing 29.79 molar per cent of ethylene chloride and 70.21 molar per cent of benzene, contains 27.2 of ethylene chloride and 72.8 of benzene.

40. Increase of the boiling-point.—Since the vapor-pressure of a solvent is depressed by the solution of a substance in it, the boiling-point must also increase, so that from this term it is also possible to define the molecular weight of the substance dissolved. It has been found empirically *that each mole of substance in solution increases the boiling-point of 1000 grams of solvent by an amount dependent only upon the nature of the solvent, and independent of the nature of the substance in solution. This constant we shall designate by the letter* $K_{b.p.}$.

The value of $K_{b.p.}$ for any one solvent can be found by experiment; or the existence of such a *boiling-point constant* can be readily shown, and its value calculated by the application of the second law of thermodynamics to the system.

Assume a very large amount of a solution in which there is 1 mole of substance to each 1000 grams of solvent.

To separate 1000 grams of pure solvent from this very large amount of solution by isothermal osmotic work at the boiling-point of the pure solvent, T, would require by definition, the work equivalent to $2T$ cals., provided the heat of solution is negligible, i.e., that no heat need be added or removed during the process to retain the temperature constant at T.

To transform this 1000 grams of liquid solvent into vapor at T would now require 1000 w_e cals.

If this work is to be done simply by the transformation of heat, it is quite evident that the heat must be absorbed at a higher temperature than T; i.e., to cause the complete separation to take place by boiling, the solution must boil at a higher temperature than the pure solvent, and just so much higher that the heat of evaporation of the pure solvent at T, 1000 w_e, can do the work $2T$ cals. We have then (p. 58),

$$\frac{2T}{1000w_e}=\frac{\Delta T}{T},$$

or

$$\Delta T_{b.p}=\frac{0.002T^2_{b.p.}}{w_e}=K_{b.p.}$$

The boiling-point constant, the increase of the boiling-point of 1000 *grams of any solvent due to the presence of* 1 *mole of substance in solution, is equal to* 0.002 *times the square of the absolute boiling-point of the solvent, divided by its heat of evaporation for* 1 *gram.*

The value of this constant, $K_{b.p.}$, is *one-tenth of that of the conventional molecular increase of the boiling-point* (which refers to 1 mole in 100 grams), and is perhaps to be preferred, for it shows more clearly than that the limitations of the boiling-point law. It will be seen from rivation that the law can only be expected to hold under the following conditions: (1) *the heat of* *n must be zero, or the solution so dilute as to make* *igible;* otherwise the osmotic work of separation e larger or smaller than $2T$ cals. per mole; (2) *re solvent alone must vaporize;* and (3) *the solution* *e so dilute that the gas laws hold, and pV really* *RT.*

urally, in calculating $K_{b.p.}$ for a solvent for which, e heat of evaporation is unknown, we can substitute ue in other terms. Thus Innes (Proc. Chem. Soc., –28, 1902) advocates the substitution for w_e of its as given above (p. 76), $w_e=\frac{\Delta p}{\Delta T}\cdot\frac{2T^2}{pM}$, and obtains

$$K_{b.p.}=\frac{0.002T^2}{\frac{\Delta p}{\Delta T}\cdot\frac{2T^2}{pM}}=\frac{\Delta T}{\Delta p}\cdot\frac{pM}{1000}.$$

re, is the change in boiling-point per unit change rnal pressure; M is the molecular weight of the t *as a gas*, while p is the pressure causing this -point. Of course Δp and p must be expressed same units.

kalotos (C. r., 144, 1104–1106, 1907) substitutes its value according to the Trouton-Nernst equa. 69, footnote) and finds

$$K_{b.p.}=\frac{M}{4750\frac{\log T}{T}-3.5},$$

from which $K_{b.p.}$ can be calculated for any solvent simply from its boiling-point and molecular weight as a gas. It also possible, of course ,to substitute for w_e its value according to the Trouton-Bingham relation (p. 69). We obtain, then,

$$K_{b.p.}=\frac{M}{\frac{8500}{T}+5.5}.$$

These two latter equations, however, will only give correct values for $K_{b.p.}$ when they give correct values for w_e, which they only do when the solvent is *unassociated.*

In general the values of $K_{b.p.}$ found by experiment agree with those calculated by the relation

$$K_{b.p.}=\frac{0.002T^2}{w_e}.$$

It will be seen that any liquid can be used as the solvent in the boiling-point method so long as it is not a solution, judged by the formation of a gaseous phase, i.e., *so long as the vapor it sends off when pure is of the same composition as the liquid it leaves behind.* (See Beckmann, Zeit. f. phys. Chem., 53, 129–137; and 58, 543–559.)

Knowing $K_{b.p.}$ for any liquid it is easy to calculate the increase of the boiling-point due to the addition of any small amount of substance dissolved in the solvent. All that is necessary is to find by a proportion from the ta the number of moles of substance in 1000 grams of lvent, and then by another proportion to find the in-ease from the known increase due to the presence of mole in 1000 grams.

Thus it is found that a solution of 2.0579 grams of dine in 30.14 grams of ether cause an increase in the oiling-point of $0^\circ.566$. What is the molecular weight f iodine in ether? $K_{b.p.} = 2^\circ.11$.

The number of grams per 1000 grams is first found rom the proportion

$$30.14:1000::2.0579:x.$$

Since M grams per 1000 gram would give an increase f $2^\circ.11$, M the molecular weight can be found from the roportion

$$x:0.566::M:2.11,$$

e., $M = 254$. Iodine in an ethereal solution, then, has e formula I_2; i.e. its formula or molecular weight in this lution is twice its atomic weight.

What is the increase of the boiling-point of 1.1 grams sugar in 76 grams of water? $K_{b.p.}$ for water is 0.52.

Since the molecular weight of sugar in water solution s 342, we have the $\frac{1.1}{342}$ mole in 76 grams of water, or x moles in 1000 grams of water, where x can be found from the proportion

$$76:1000::\frac{1.1}{342}:x.$$

Then since 1 mole of sugar in 1000 grams of water would increase the boiling-point 0°.52, our increase must be y in

$$1:x::0.52:y,$$

where $y=0^\circ.022$.*

For the method of determining the boiling-point and its increase see Getman's "Laboratory Exercises in Physical Chemistry," Ostwald-Luther's "Physiko-chemicher Messungen," or Findlay's "Practical Physical Chemistry."

41. Depression of the freezing-point.—More than one hundred years ago Blagden found by experiment that the freezing-point of a solvent is depressed by the addition of any substance to it.

Just as for the boiling-point increase it has been found empirically that *each mole of substance in solution depresses the freezing-point of* 1000 *grams of solvent by an amount dependent only upon the nature of the solvent and independent of the nature of the substance in solution. This constant we shall designate by the letter* $K_{f.p.}$. And this $K_{f.p.}$ can also be found either by experiment or by a calculation based upon the second law of thermodynamics.

---

* The molecular weight or the increase of the boiling point can also be found in one operation by aid of the equation. $M=1000K_{b.p.}\frac{g}{G\Delta}$, where g represents the grams of substance, G the grams of solvent, Δ the increase, and M the molecular weight of the dissolved substance, but the above method will be found much easier to remember.

It can also be shown qualitatively and very simply that since the addition of substance to a liquid lowers its vapor-pressure it must also lower its freezing-point.

Since the ice which is separated is the pure solvent, and the freezing-point is that temperature at which both solid and liquid may exist together in equilibrium in all proportions, the vapor-pressure of ice and liquid must be the same. This has already been proven, and if it were not true a perpetual motion would be possible. In Fig. 11 *ww* is the vapor-pressure curve for water, *ss* that for a solution, and *ii* that for ice. At the point $t=0$ ice and water have the same vapor-pressure, and so are in equilibrium. The solution and ice, however, can only be in equilibrium at the temperature corresponding to the intersection of the two curves, *ii* and *ss*, for only there will the vapor-pressure be the same, i.e., the freezing-point of the solution, where ice and solution can exist

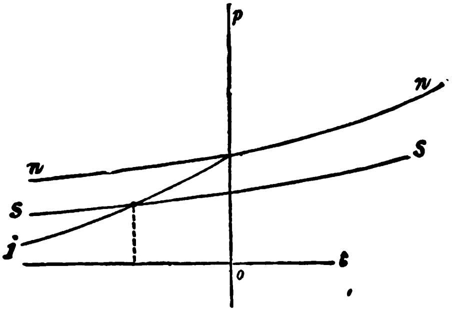

FIG. 11.

together in equilibrium, must lie below that of pure water. The more substance in the solution, the lower the vapor-pressure curve will be, and the lower will be the point of intersection and the freezing-point.

The quantitative relation between freezing-point depression and concentration of dissolved substance can be derived just as was that for the boiling-point increase.

Assume a very large amount of a solution in which there is 1 mole to each 1000 grams of solvent.

To separate 1000 grams of pure solvent from this very large amount of solution by isothermal osmotic work at T, the freezing-point of the pure solvent would require, by definition, the work equivalent to $2T$ cals., provided the heat of solution is negligible, i.e., that no further heat need be added or removed during the process of separation to retain the temperature constant at T.

The freezing of this 1000 grams of solvent would evolve at T $1000\,w_f$ cals.

If now this work of separation is to be done simply by the transformation of heat, it is quite evident that the heat must be evolved at a lower temperature than T, i.e. to cause the complete separation by freezing out the 1000 grams from the solution, the solution must freeze at a lower temperature than the pure solvent, and jus so much lower that the heat of fusion, which is $1000w_f$ a T, can do the work $2T$ cals. We have, then (p. 58),

$$\frac{2T}{1000w_f}=\frac{\varDelta T}{T},$$

or

$$\varDelta T_{f.p.}=\frac{0.002T^2_{f.p.}}{w_f}=K_{f.p.}$$

The freezing-point constant, the depression of the freezing-point of 1000 *grams of any solvent due to the presence of* 1 *mole of substance in solution, is equal to* 0.002 *times the square of the absolute freezing-point of the solvent, divided by its heat of fusion for* 1 *gram.*

The value of this $K_{f.p.}$ is also *one-tenth of the conventional molecular freezing-point* constant, and also indicates more clearly the limitations of the method.

This law, from its derivation, can only hold rigidly under the following conditions: (1) *The heat of solution must be zero, or the solution must be so dilute that the heat of solution is negligible,* otherwise the osmotic work of separation will be larger or smaller than $2T$ cals; (2) *the pure solvent, alone, must separate as solid phase;* and (3) *the solution must be so dilute that the gas laws hold, i.e., pV must equal RT.* (See Bancroft, Jour. Phys. Chem., 10, 319, 1906.)

Just as with the boiling-point the values of $K_{f.p.}$ found by this equation agree in general with those experimentally determined.

It will be seen that any liquid can be used as the solvent in the freezing-point method so long as it is not a solution, *judged by the formation of a solid phase, i.e., so long as the solid separating from the pure solvent has the same composition as the liquid it leaves behind.* (See Morgan and Benson, Jour. Am. Chem. Soc., 29, 1168–1175, 1907, and Morgan and Owen, *Ibid.*, 29, 1439–1442, 1907.)

It is also simpler in calculating molecular weights from the freezing-point depressions to use two proportions rather than the formula usually employed.* What is the molecular weight of acetic acid in water? 0.681 gram in 100 grams of water causes a depression of the freezing-point of 0°.2168; $K_{f.p.}$ for water is 1.89.

Since there are 0.681 gram in 100 grams of water there must be 6.81 grams in 1000 grams of water, and we have

$$M : 1^\circ.89 :: 6.81 : 0^\circ.2168,$$

hence M the molecular weight of acetic acid in water solution is 59.4.

What is the freezing-point of 3.45 grams of glucose in 65 grams of water? The molecular weight of glucose is 180 and $K_{f.p.}$ for water is 1.89.

3.45 grams of glucose in 65 grams of water would be x grams in 1000 grams of water, where x can be found from the proportion

$$3.45 : 65 :: x : 1000.$$

---

* $M = 1000 K_{f.p.} \frac{g}{GJ}$, see p. 172, foot-note.

We must have, then, $\frac{x}{180}$ moles of glucose in 1000 grams of water, and the freezing-point depression will be y in

$$1:1^\circ.89::\frac{x}{180}:y^\circ,$$

$$y=0^\circ.558.$$

Dawson and Jackson (Trans. Chem. Soc., 93–94, 344–350, 1908) have shown that the lowering of the transition temperature of a solvent, i.e., the temperature at which one solid modification of the solvent is transformed into another, can also be used just as the freezing-point for the estimation of molecular weight in solution.

The apparatus for the determination of the freezing-point (or transition point) was devised by Beckmann and is shown in Fig. 12. In the freezing-tube *A* the solvent (15—30 cc.) is introduced and a freezing-mixture (ice and salt) is placed in *C*. The temperature is allowed to fall until the liquid is overcooled 1 or 2 degrees; then is it stirred, ice forms, and the thermometer rises to the true freezing-point and remains constant. The cause of the rise in temperature is the sudden formation of ice, which gives up heat to the liquid. *B* is a tube which acts as an air-bath and causes the cooling to take place more evenly. After the freezing-point of the pure solvent is determined the solution is introduced and the process repeated. Or the solution may be made in the tube by dropping a weighed amount of solute into the known amount of the solvent.

One point to be kept in mind is that the freezing-point thus determined is of a solution which is more concentrated than the one started with, for some of the solvent has been removed by the freezing. This follows from the fact that the freezing-point is that temperature at which ice and solution exist together in equilibrium. The concentration of the solution

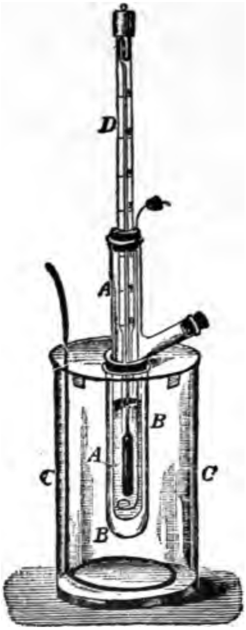

FIG. 12.

due to the separation of ice may be calculated from the overcooling (see p. 111), for it has been found for water that for each degree of overcooling 12.5 grams of water separates from each liter. Each degree of overcooling, then, causes the solution to be 1/80 more concentrated than the original one. If the solution is dilute, we may find the freezing-point of the original solution by a proportion. Thus if the overcooling is 1°, the depression of the freezing-point 0.1, and v represents the volume of solution, we have

$$v:(v-\tfrac{1}{80}v)::0^\circ.1:x,$$

where x gives us the depression of the freezing-point caused by the solution of the weighed amount of substance in the volume v, i.e., in the volume of solvent present before the separation of solid.

Or, and this will hold for concentrated as well as dilute solutions, we may calculate from the overcooling the real strength of the solution in equilibrium with ice, i.e., the solution whose freezing-point we have actually determined (see also p. 111).

Thus in the illustrative example on page 176 suppose the overcooling had been 2°. Each degree would have caused the separation of $\frac{1}{80}$ of the water present, consequently in this case, in place of really having 0.681 gram of acetic acid in 100 grams of water, we would have 0.681 grams in $(100-100\frac{1}{40})$ grams, which must be calculated to 1000 grams of water and then used in the proportion.

All these overcooling difficulties may be avoided by using the simple method proposed by T. W. Richards (Jour. Am. Chem. Soc., 25, 291–298, 1902).

Here the temperature of a mixture of the solid and liquid phases is noted after equilibrium has been established. Then a solution of the substance added, the whole system, stirred, and the thermometer read again. By analyzing a sample of the liquid phase, withdrawn by a pipette from the vicinity of the thermometer bulb, the strength of the solution, of which the freezing-point depression has been read, is finally found. This method is especially valuable when by the Beckmann method the solid separated might contain solute as well as solvent.

Lewis (J. Am. Chem. Soc., 30, 668–683, 1908) considers the freezing-point method to be even better than that depending upon vapor-pressure for the indirect determination of osmotic pressure. The formula he derives for this purpose for aqueous solution is

$$P = 12.06\Delta - 0.021\Delta^2,$$

when P is the osmotic pressure in atmospheres and Δ is the depression of the freezing-point in centigrade degrees.

42. Electrolytic dissociation or ionization.—The mor weights of a very large number of organic sub- :s in water are found correctly from the osmotic ıre and the other methods mentioned above, i.e., :orrespond to the values in the gaseous state. For substances, however, varying results are obtained. ›smotic pressures, freezing-point depressions, boiling- increases, and vapor-pressures are here always too and consequently from our definitions the molecular ıt is smaller than that observed in the gaseous state. reminds one immediately of the abnormal densities ses. In the case of the gas the volume increases and ressure is constant; in that of the solution, however, olume remains constant, while the osmotic pressure ges.

henius, in attempting to find an explanation for the rmal osmotic pressures, found by experiment that *substances, and only those, which give abnormal ic pressures in solution are capable of conducting lectric current, and if they are dissolved in other nts in which they behave normally they lose this power.* rhenius determined the electrical conductivity of ubstance in terms of molecular conductivity. The cular conductivity of a solution being defined as eciprocal of the resistance (in ohms) of the volume quid which contains one formula weight of the sub- e, i.e., the weight of the generally accepted formula, electrodes being 1 cm. apart and large enough to contain between them the entire amount of solution. This value, naturally, is not found directly, but is calculated from that value found for a centimeter cube of the solution. (See Chapter IX.) In this way, always having 1 mole (according to the accepted formula) between the electrodes, he found that the more dilute the solution the greater is the molecular conductivity. In many cases, indeed, he was able to reach such a dilution that the molecular conductivity attained a maximum value, which is unaffected by further dilution. This molecular conductivity at infinite dilution, as it is called, is designated by the term μ_∞, that value for any dilution V, being designated by μ_v.

From this it is apparent that the solution undergoes some kind of a change as the result of dilution; and the investigation of such solutions at various dilutions shows, indeed, that the molecular weight (according to definition) also changes with the dilution; the molecular weight decreasing to a minimum constant value, which, for binary electrolytes, is one-half the formula weight of the substance dissolved. It is not unreasonable, then, to infer that the breaking down of the formula (and consequently of its weight) of the substance in the solution is very intimately connected with the power it possesses of conducting the electric current.

These facts formed the starting point of what is known at present as the "theory of electrolytic dissociation."

As this theory to-day is much misunderstood by many, and is the subject of much speculation on the part of others, it will be necessary for us to consider carefully just what is fact and what assumption, and to see clearly which portions are hypothetical, and which are destined to remain under any hypothesis or lack of hypothesis; in other words, which are experimental facts. It may be said, however, that that which is hypothesis in this theory is unessential, as far as the use of the data is concerned, and the only hypothesis present, as we shall consider it, is that inherent in the terminology, which is a relic of the atomistic hypothesis and so utterly beyond our power either to prove or disprove.

The salient facts which have been grouped in this theory, for it is a theory in the sense that it is a law of nature holding between certain limits, although these are not as yet definitely fixed, are as follows:

(1) The molecular conductivity of certain substances in water is found to increase up to a maximum, constant value, and this increase is the result of dilution.

(2) Those solutions which conduct the current also give abnormal osmotic pressures, freezing-point, boiling-points, and vapor-pressures; in other words, the molecular weight (according to the above definitions) decreases with increased dilution and finally reaches a minimum value, which, for binary electroyltes, is one-half the accepted formula weight of the substance.

(3) Those substances which in water conduct the current and give abnormal osmotic pressures, depressions of the freezing-point and vapor-pressure, and increases of the boiling-point, give normal osmotic pressures, etc., when dissolved in other solvents in which they do not conduct.

(4) The nearer the value of μ_v is to that of μ_∞, the more abnormal the value of the osmotic pressure, etc. (formula weight), of the solution. And the solution for which μ_∞ is found also gives the maximum osmotic pressure, i.e., the minimum molecular or formula weight.

(5) The molecular conductivity of a solution at infinite dilution is an additive value, i.e., is equal to the sum of the conductivities of the substances of which it is composed. The meaning of this is as follows: The molecular conductivity at infinite dilution of, for example, potassium chloride plus that of nitric acid minus that of potassium nitrate is found to be equal to that of hydrochloric acid. In other words,

$$\mu_\infty \mathrm{KCl} + \mu_\infty \mathrm{HNO_3} - \mu_\infty \mathrm{KNO_3} = \mu_\infty \mathrm{HCl}.$$

For this to be true, and it is true in general for all substances, it is necessary that the molecular conductivity of each substance in solution be the sum of two values which are independent each of the other. Chlorine, for example, as the constituent of an electrolyte, at the dilution giving μ_∞, has the same conducting effect when part of a compound with one element as it has when combined with any other. It is possible, then, to find the value of μ_∞ for any binary electrolyte when the values for the elements composing it are known. In other words, the conductivities of the solution as produced by the presence of any element can be calculated; and from these values, by summation, the value of μ_∞ for any binary electrolyte can be found.

(6) When a solution is electrolyzed, the products of electrolysis appear instantaneously at the electrodes so soon as the circuit is completed. This indicates (since the solvent, water, does not conduct beyond a very small extent) that whatever does carry the current through the liquid is charged with electricity even before the current is applied, for the conduction is due to the dissolved substance, and the speed of movement of the substance can be measured, so that it is no question of matter being electrically charged at one electrode before carrying this charge bodily through the solution to the other. (See Chap. IX.) Further, it is observed that the same amount of electricity, 96537 coulombs, is necessary for the separation of one equivalent weight (in grams) of any element; in other words that 96537 coulombs of electricity are transported through the liquid with each equivalent weight (in grams) of an element deposited. (Faraday's Law, see Chapter IX.)

(7) The properties of electrolytes are found to be the

sum of the properties of the products observed during electroylsis. Thus any solution giving off chlorine on electrolysis, excluding secondary reactions, will precipitate silver from its solution as the chloride. And if chlorine cannot be produced in any way by the electrolysis, silver will not be precipitated as chloride from its solutions. And, on the other hand, silver is only precipitated by chlorine when contained in a solution from which silver can be deposited by the current by primary action.

The catalytic effect of acids on the inversion of sugar as well as on the decomposition of methyl acetate, is found to be proportional to the ratio $\frac{\mu_v}{\mu_\infty}$ for the acid; and when a large amount of a salt of this acid is added to the acid this effect is decreased. But this is only true when the salt added is an electrolyte.

All copper solutions, when very dilute, show the same blue color, and this also depends upon the ratio $\frac{\mu_v}{\mu_\infty}$, and can also be changed, as the effect of acids were above, by the addition of a large amount of an electrolyte which contains the same acid radical as the copper salt in question.

(8) Observation shows that when an element is separated on one electrode, anode or cathode, it is always separated on that one by primary action; in other words, the sign of the electricity transported by an element is

always the same.* Unless an element in the pure state, when dissolved in water, reacts with the water it does not conduct the current. This circumstance is assumed to be due to the fact that only one kind of electricity could be carried by the substance, and hence it produces no conduction.

The question now arises as to what theory can be found to correlate these facts and observations so that the generalization thus obtained may be employed to foresee other facts, and applied to other observations that they, in their turn, may be elucidated and generalized. By the word theory, then, we do not mean a hypothesis, in which something not observed is added to the facts to "explain" them, but only a generalization of observed facts. In other words, what law of nature, holding within definite, if narrow, limits, can be obtained from the above experimental facts when considered together?

The generalization which has been made from these facts is known as the theory of electrolytic dissociation, and, considering those portions which are free from hypothesis and fulfil the above conditions, (in other words, omitting the hypothetical portions which it has attained since the time of its inception), we find in it, within certain limits, a definite law of nature.

The principal points of this theory are summarized below in brief form, and will each be expanded in the later portions of the book.

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* See Le Blanc, Z. f. Elektrochem., 11, 813–818, 1905.

A substance in solution, which conducts the electric current, is dissociated or ionized into its constituents, and these constituents, when secondary actions are excluded, appear at the electrodes during electrolysis. The extent of the ionization or dissociation in any solution being given at the dilution V (number of liters in which 1 mole is dissolved) by the ratio $\frac{\mu_v}{\mu_\infty} = \alpha$.

These products of ionization or dissociation are charged with electricity, 96537 coulombs being carried by the gram equivalent of any element (see (6) above). A further proof of this charged state of ionized matter is given by the fact that not only is the current carried by a solution dependent upon the number of gram equivalents transported, but, as we shall see later, any other means of depositing the constituents of the solution upon the electrodes liberates an amount of electricity which depends also upon the number of gram equivalents deposited. And all cells in order to give a current must contain electrolytes, i.e., solutions which are ionized.

Since a solution which by conductivity is shown to be completely ionized, or practically so, leads to a molecular weight, by osmotic pressure or any of the other methods, of one-half the value expressed by the formula weight, then, from the case of hydrochloric acid in solution, where the formula weight of the hydrogen and chlorine in the ionic state, according to our definition of molecular weight, must be synonymous with the atomic weight.

The ionic state, then, is an allotropic form of the ordinary state of the constituents, and differs from that in being charged with electricity, in having less energy than when in the gaseous state, and in always being transformed into the ordinary state on the loss of its charge of electricity.

Since the constituents in the case already mentioned, and in general in all cases, show a molecular weight (by the definition) which is the same as the atomic weight, it is possible to determine α, the degree of ionization, by osmotic pressure, etc., measurements, or from the average molecular weight of the substance in solution, as determined by osmotic pressure or any of the other methods. If, for example, we start with one formula weight of hydrochloric acid in a solution, and α moles of it are ionized, the total number of moles will consist of $(1-\alpha)$ of un-ionized HCl and α moles each of $H^{\cdot}$ and Cl' (where the dot indicates positive electricity as the charge, and the accent negative). The total number of moles in the volume of the solution will go then from 1 to $(1-\alpha)+2\alpha$, i.e., to $1+\alpha$, and the ratio of osmotic pressures when entirely un-ionized to that when partially ionized will be the same as this. In other words, if the formula weight in a certain volume *should* give the osmotic pressure P', it will give, when ionized to the extent α, the pressure $P=(1+\alpha)P'$. Since the number of moles (by definition) shown by the same weight is thus increased, the molecular weight will be smaller, and we have as the relation between the two values of the molecular weight: $M'(1+\alpha)=M$, where the M refers to substance if it were un-ionized, i.e., is the formula weight of the substance, and M' is the average molecular weight observed.

Just as with gaseous dissociation, the ionization of a solution is affected by the presence of one of the products of the dissociation, and later when we consider the quantitative effect of this for gases, we shall also consider it for solutions.

Owing to the fact that the dissociated constituents in a solution were called ions (in the Faraday sense of charged atoms), it has become common to speak of and to represent the ionized state as though it were characterized by an atomic structure; in other words, as if it existed as an accumulation of charged particles of infinitesimal size. As this is pure hypothesis, and cannot be either proven or disproven, *we shall only use the word ion here in the sense that it is expressive of the relation* $\frac{\mu_v}{\mu_\infty}$, *i.e., we shall only use it in the sense of ionized matter, according to this definition, and as purely expressive of an experimentally determined fact.*

Summarizing our argument, the application of the experimental definitions of formula or molecular weight in solution (derived as given above) indicates that certain substances are decomposed in certain solvents, the fraction decomposed being α in the expressions $M'(1+\alpha)=M$ according to any of the methods) and $\alpha=\frac{\mu_v}{\mu}$, and increasing with the dilution up to the value which, for binary electrolytes, gives $M=2M'$. In general, for other than binary electrolytes, we have just as on page 23,

$$[(1-\alpha)+i\alpha]M'=M,$$

where at the maximum dilution we have

$$i=\frac{M}{M'}.$$

That this is really the result of a decomposition, and not merely the failure in these cases of the definitions of formula weight in solution, is evidenced by the above facts and many others, given later. And that this ionized matter which is formed is electrically charged is also not to be doubted, as well from the above facts as from the general agreement of the results by electrical and other methods.

It is always to be remembered, then, that when we speak of ionization we mean something which can be defined in terms of experiment, and is free from hypothesis And the same is true of ionized matter, so long as we do not assume for it a certain structure as might be natural from the all too common expressions "an ion" or "the ions." In order to avoid this difficulty we shall speak of copper ion, chlorine ion, etc., meaning simply an amount of ionized copper or of ionized chlorine, and never of copper ions or chlorine ions, which is hypothetical.

Later we shall find that starting with this definition of ionized matter in a simple substance we can derive other experimental definitions, not only for ionization in general but also for the amount of any one definite kind of ionized matter which is present with any number of other kinds.

One fact may be mentioned here which indicates what a very marked difference dilution makes in the behavior of a substance, and which decidedly supports the conclusions we have just drawn. Although hydrochloric acid is more volatile than hydrocyanic acid, it has been observed that from a mixture of the dilute acids (0.1 molar of HCl) it is possible to distil the HCN quantitatively (provided the dilution of the HCl is retained at about this value by the frequent replacement of the water lost). In the light of the above theory the difference between the two acids in solution is that while $\frac{\mu_v}{\mu_\infty}$ is nearly equal to 1 for HCl, it is very small for HCN. In other words, HCl is composed principally of the ionized constituents $H^{\cdot}$ and Cl', which cannot produce HCl gas without going through the state HCl in solution, and that is prevented by the nearly constant dilution which is retained during the distillation. Any gaseous substance then, which in solution is largely ionized, is more difficult to distil than an un-ionized or less ionized one. The HCN, being dissolved and retained in this state in solution, can be expelled readily just as any other gas which undergoes no great change in solution. This method, indeed, was discovered as the result of such theoretical reasoning, and it is but one example of the many practical applications of the above generalization. (For details of the separation see Richards and Singer, Am. Chem. J., 27, 205, 1902).

It is not to be imagined that the facts mentioned above are the only ones leading to these conclusions, for later, throughout our work, we shall find occasion to consider other things which will confirm each of the steps leading to the final conclusion. In other words, it is not to be thought that the whole theory has been described in this place, or that, because some of the points mentioned are not clear, the theory itself is to be condemned, for many of the points can only be brought out after considering certain other methods which will enlarge our horizon. It may be said, however, that these further aids but confirm and make more evident the truth of the conclusions we have arrived at. At the same time we must not forget that we have been speaking of this subject as lying within certain limits, and so cannot expect our conclusions to hold outside of them, nor to condemn them because they do not. The relation of substances in non-aqueous solvents to a certain extent is different, and consequently these conclusions could not be expected to hold. As a matter of fact, the conduction relations for these solutions are so utterly different from the aqueous ones that it would be impossible to consider them together at all in the light of our present knowledge. All of these points will be discussed more fully later, however, and the limits stated, within which our conclusions in general will hold. It is to be remembered, however, that simply because our theory does not hold for solutions in certain non-aqueous solvents (solutions which show no similarity in behavior to the aqueous ones, and which may or may not be solutions, as we consider them, but may involve an entire rearrangement of the composition of the solvent, or solute, or both), it should not be considered as false and of little use. For the two kinds of systems are so different that it would be impossible to imagine that both are subject to the same laws.

The value for α, the degree of ionization for a few electrolytes is given below for varying conditions. These are the values as found from the ratio of molecular conductivities, since that method is the most delicate one for this purpose which we possess.

V	$AgNO_3$ 25° a
16	0.828
64	0.899
512	0.962
	40°
16	0.832
64	0.904
512	0.965

V	$AgNO_3$ 60° a
16	0.841
64	0.909
512	0.964
	HCl 25° a
2	0.876
16	0.955

V	HBr 25° a	HI 25° a
2	0.897	0.895
4	0.932	0.926
8	0.950	0.945
16	0.965	0.963

V	KCl 25° a	NaCl 25° a	NH_4Cl 25° a	LiCl 25° a
2	.....	0.737	.....	.....
10	0.86	0.842	0.852	0.803
100	0.94	0.937	0.94	0.907
1000	0.98	0.982	0.979	.....
10000	0.993	.....	.....	.....
16667	0.996	.....	.....	.....

For further information of this sort, see Rudolphi, Zeit. f. phys. Chem., 17, 385, 1895; Jones and West, Am. Chem. J., 33, 357–422, 1905; and Noyes, Carnegie Publication No. 63, 340, 1907.

Certain general relations have been observed connecting the extent of the ionization of salts of the same type, and also connecting the ionization of salts of different types, which are very convenient approximations. Thus Noyes and Melcher (Carnegie Publication, No. 63, 29) show the following rough proportionality between the un-ionized fraction of a salt at any concentration and the product of the valences of its ions. In the table below, under *A*, are given the mean values of the percentage of un-ionized salt, 100 $(1-\alpha)$ for the neutral salts of each type at the concentration 0.04 moles per liter and for the one-one salts at 0.08 moles per liter, and under B are given the ratios of these values to the product of the valences (V_1, V_2) of the ions.

V_1V_2	Moles per Liter.	18°		100°		156°		218°		281°		306	
		A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
1×1	0.04	12	12	15	15	17	17	20	20	25	25	31	31
1×1	0.08	15	15	18	18	21	21	25	25	31	31	39	39
1×2	0.04	28	14	34	17	40	20	51	25	65	32	74	37
2×2	0.04	55	14	68	17	81	20	93	23	—	—	—	—

Examples of the three types illustrated here are KCl (1–1), $BaCl_2$ (2–1), and $MgSO_4$ (2–2). When the comparison is made at the same equivalent concentration here (i.e., the 0.08 for the 1–1), the principle seems to hold satisfactorily, even at the high temperature when the ionized portion is reduced to 26% for the 1–2 salt and to 7% for the 2–2 salt.

Another and similar relation to this is given by Bodländer, with Storbeck and Eberlein (Zeit. f. anorg. Chem., 31, 19, and 39, 195). According to this the ionization of any salt is equal to that for a 1–1 salt, *at the same* EQUIVALENT *dilution, raised to a power equal to the product of the valences of the ions of the salt whose ionization is to be determined.*

Examples of this relation are given in the tables below, all dilutions being *equivalent normal.*

Dilution (Liters per Equivalent).	100	20	10	2
α-ionization of KCl	0.94	0.88	0.85	0.78
α^2	0.88	0.77	0.73	0.61
Ionization of $BaCl_2$	0.87	0.77	0.74	0.60

Liters per Equivalent.	KCl	Na_2SO_4		$K_3Fe(CN)_6$		$K_4Fe(CN)_6$		$Na_6C_{12}O_{12}$	
	α	α'	α^2	α'	α^3	α'	α^4	α'	α^6
32	0.90	0.81	0.81	0.75	0.74	0.67	0.67	0.50	0.55
64	0.93	0.86	0.87	0.80	0.80	0.74	0.74	—	—
128	0.95	0.90	0.90	0.85	0.85	0.81	0.81	0.65	0.73
256	0.96	0.92	0.92	0.89	0.89	0.87	0.87	—	—
512	0.97	0.94	0.94	0.92	0.92	0.91	0.89	0.74	0.83
1024	0.98	0.96	0.96	0.95	0.94	0.94	0.93	0.89	0.89

Here α' is the actually determined value; α^2, α^3, α^4, and α^6 being the values of α for KCl raised to a power in each case equal to the product of the valences of the ions formed from the salt. Thus we have $2Na^{\cdot}$ and SO_4'' (1×2); $3K^{\cdot}$ and $Fe(CN)_6'''$ (1×3); $4K^{\cdot}$ and $Fe(CN)_6''''$ (1×4); and finally $6Na^{\cdot}$ and $C_{12}O_{12}''''''$ (1×6); the concentrations for the $1/32$ normal being $\frac{1}{2}(1/32Na_2SO_4$; $\frac{1}{3}(1/32K_3Fe(CN)_6)$; $\frac{1}{4}(1/32K_4Fe(CN)_6)$; and $\frac{1}{6}(1/32Na_6C_{12}O_{12})$. Whether this relation holds at other temperatures and for other salts is apparently not as yet known; if it does it is certainly a very valuable relation.

43. The relations existing between osmotic pressure, vapor pressure, freezing-point and boiling-point, and the effect of ionization upon these quantities.—Although it is possible to find mathematical relations connecting the osmotic pressure with the vapor-pressure, or freezing-point, etc., it will be seen that any one of them may be calculated from any other by calculating back from the given value the concentration in moles per liter of the solution, for any of the values can be calculated when the concentration of solute is known. Thus the freezing-point of a water solution is 0°.3 below that of the pure solvent. What is the vapor-pressure of the solution at 0°, the vapor-pressure of pure water at 0° being 4.57 mm.?

Since 1 mole per liter of solvent would depress the freezing-point 1°.89 ($=K_{f.p.}$) this solution must contain

$$1^\circ.89 : 0^\circ.3 :: 1 : x,$$

x moles per liter. The vapor-pressure then, from $\frac{p'}{p}=\frac{N}{N+n}$, is

$$p'=4.57\frac{\frac{1000}{18}}{\frac{1000}{18}+x}\text{mm.},$$

for 1000 grams of water is equal to $\frac{1000}{18}$ moles.

When a depression of the vapor-pressure is given, i.e., $p-p'$ in the formula $\frac{p-p'}{p}=\frac{n}{N+n}$ or $\frac{p-p'}{p'}=\frac{n}{N}$, all we can find is the relation between the number of moles of solute (n) and those of solvent (N). But by fixing the amount of solvent, 1000 grams, for example, and owing its molecular weight as a gas, we can solve e equation for the concentration of solute in that quantity solvent, and then from this calculate the osmotic ressure, freezing-point or boiling-point of the solution.

Thus the vapor-pressure of a solution is $\frac{9}{10}$ that of e pure solvent (water) at 0°, what is the freezing-point lepression of the solution? Since $\frac{p'}{p}$ in $\frac{p'}{p}=\frac{N}{N+n}$ is qual to 0.9, we have

$$0.9=\frac{N}{N+n}=\frac{\frac{1000}{18}}{\frac{1000}{18}+n},$$

here n is the number of moles of solute in 1000 grams f solvent. The depressions of the freezing-point is erefore $n\times 1°.89$.

It now simply remains for us to express analytically e effect of ionization upon the osmotic pressure, de-ressions of the freezing-point and vapor-pressure, and crease of the boiling-point; for the definitions of for-ula weight in terms of these methods have already en stated, and the derivation of the concept of ioniza-n traced from them.

Naturally, if in place of n moles per liter of solvent have after ionization $n[(1-\alpha)+i\alpha]$, where i is the mber of moles of ions from 1 mole of salt by complete ionization, the osmotic pressure can be found from the proportion

$$n:n[(1-\alpha)+i\alpha]::n\left(22.4\frac{273+t}{273}\right):P',$$

where P' is the osmotic pressure at t° of the n moles in 1 liter of solvent, ionized to the extent α into i ions.

The freezing-point depression is $\Delta_{f.p.}$ in the proportion

$$n:n[(1-\alpha)+i\alpha]::nK_{f.p.}:\Delta_{f.p.},$$

where n and $n[(1-\alpha)+i\alpha]$ refer to moles per 1000 gram of solvent.

The boiling-point increase is $\Delta_{f.p.}$ in the proportion

$$n:n[(1-\alpha)+i\alpha]::nK_{b.p.}:\Delta_{b.p.},$$

when n and $n[(1-\alpha)+i\alpha]$ also refer to moles per 1000 grams.

And the vapor-pressure is p' in the relations

$$\frac{p-p'}{p}=\frac{n[(1-\alpha)+i\alpha]}{N+n[(1-\alpha)+i\alpha]}, \qquad \frac{p-p'}{p'}=\frac{n[(1-\alpha)+i\alpha]}{N},$$

or

$$\frac{p'}{p}=\frac{N}{N+n[(1-\alpha)+i\alpha]},$$

where $N=\frac{1000}{M}$, M being the molecular weight of the *solvent as gas.*

At complete ionization into two ions, then, the osmotic pressure, depression of the freezing-point, and increase of the boiling-point would all be doubled, while the vapor-pressure would only be affected by the value of *n* being doubled.

44. Division of a substance between two non-miscible solvents. Depressed solubility.—If a water solution of succinic acid is shaken with ether, the acid is divided between the two solvents in such a way that there is always a certain ratio between the two concentrations, independent of the relative amounts of the two solvents. Table IV shows this.

TABLE IV.

H_2O (1).	Ether (2).	In H_2O (3).	In Ether (4).	Coefficient (5).
70 cc.	30 cc.	43.4	7.1	6 almost
49 cc.	49 cc.	43.8	7.4	6 "
28 cc.	55.5 cc.	47.4	7.9	6 exact

Columns 3 and 4 give the number of cc. of a $Ba(OH)_2$ solution which is necessary to neutralize 100 cc. of the solutions.

If there are two or more substances in solution the coefficients of partition are the same as if each substance were present alone.

The solvent behaves here with respect to the substance dissolved just as it would to a gas, i.e., between the two parts (liquid and solution) there is a certain coefficient of absorption—the concentration of substance acting as the pressure of the gas, and the temperature having the same influence in both cases.

If the relation of the molecular weights remains the same throughout the various concentrations employed, the coefficient of partition will remain constant. Thus *p*-nitrophenol shows a coefficient of partition $\left(\frac{C_{ch}}{C_w}\right)$ in the system water-chloroform, which increases with the temperature and concentration and indicates that the *p*-nitrophenol is normal in molecular weight in water and is polymerized in chloroform solution. In dilute solution the polymerization is very inconsiderable, however. In few words, speaking from the experiments, this means that the greater the amount of *p*-nitrophenol in the system and the higher the temperature, the greater is the proportion dissolved by the chloroform, and this variation has nothing to do with the solubility variations with the temperature of the solvents when used alone.

An interesting application of this was made by Morse (Zeit. f. phys. Chem., 41, 722, 1902) to find the amount of $HgCl_2$ remaining uncombined in a complex equilibrium By finding the coefficient of partition of $HgCl_2$ between water and toluol for known amounts of $HgCl_2$, and then that for $HgCl_2$ between the aqueous complex solution and toluol, he was able to find the amount of $HgCl_2$ which was free and capable of dissolving from the complex solution. (For the quantitative relation existing between the molecular weights in the two solvents and the coefficient of partition, as well as the uses of this very important method, see Chapter VIII.)

If one solvent is soluble in another the amount of the one dissolved will depend upon its state, i.e., whether it is pure or contains a substance in solution. Just as with solids, we have for liquids a certain solution pressure, i.e., a force which causes them to dissolve. In the same way that the vapor-pressure is depressed by the addition of a substance, so is the solubility of one liquid in another. This follows from the analogy between gases and substances in solution. If s is the solubility of A, i.e., the amount of A in the unit of volume of B, and s' is the solubility of the same after an addition of substance to A, then in analogy to

$$\frac{p-p'}{p'}=\frac{n}{N}$$

we have

$$\frac{s-s'}{s'}=\frac{n}{N},$$

where N is the number of moles of solvent A and n the number of moles of solute in A.

This was first deduced by Nernst, who used the formula as a method for the determination of the molecular weight.

If an excess of ether is agitated with water and the freezing-point of the mixture determined it is found to be lower than that for pure water. If the ether contains an amount of substance which is insoluble in water, then its solubility in water will be decreased, and the freezing-point of the mixture will be higher than before. Calling this difference the molecular increase of the freezing-point, when the dissolved ether itself contains 1 mole of dissolved substance, we have the simple relation

$$m=k'\frac{w}{t-t'},$$

where m is the molecular weight of the substance dissolved in ether, w is the weight of this in 100 grams of ether, t is the freezing-point of a saturated aqueous solution of ether, t' the freezing-point of the saturated aqueous solution of ether containing w grams per 100 grams, and k' is this molecular increase of the freezing-point, just defined. The value of k' for a water-ether system (it varies with each system) is 3.06.

Table V gives a few results of this method. The benzene and naphthalene are the substances which in each case are dissolved in the ether

TABLE V.

Substance.	w	$t-t'$	m (cal.)	m (found)
Benzene............	2.04	0.080	78	77
	5.87	0.219	78	82
Naphthalene........	3.42	0.082	128	128

t in all cases is equal to $-3°.85$, i.e., the freezing-point of a saturated solution of ether in water. The solution of substance in ether is here slightly increased in concentration, owing to the separation of the ether with the ice, but, as very strong ethereal solutions are rarely used, it has but little influence. Other substances than ether may also be used with water, the constant k' of course being different for each one. Other results and the calculation of the value of k' which transforms freezing-point results into those of solubility must be sought in the original paper. (Nernst, Zeit., f. phys. Chem., 6, 16 and 573, 1890).

45. Solid solutions.—Solid solutions, which have already been considered in the previous chapter, are homogeneous solid phases which can vary continuously within certain limits. These limits are smaller for solids than they are for liquids, just as the limits for these are much more restricted than for gases. The most important differences between a solid solution and a mixture of solids are as follows: Work is necessary to separate the constituents of the solution, and consequently these do work in uniting to form the solution; a solution has a lower vapor-pressure than the pure solvent; and a solution has a smaller solubility in all liquids than the pure solvent. Examples of solid solutions are given by mixtures of isomorphous crystals; zeoliths, i.e., natural water holding silicates, which lose water and yet retain their transparency, although the vapor-pressure is reduced; hydrogen with palladium; hydrogen with iron; and mixtures of two crystalline substances which have different forms, but which give a mix-crystal like that of the substance present in excess. The reader must be referred for further information on this subject to one of the books treating it in detail, Findlay's Phase Rule, for example.

46. Colloidal mixtures.*—Colloidal mixtures, for convenience, are divided into two classes. Of these we shall consider *colloidal solutions*, the type of which is a solution of gelatine, and *colloidal suspensions*, of which arsenious sulphide is a type.

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* For further information the reader is referred to a paper by Noyes (Jour. Am. Chem. Soc., 27, 85, 1905), of which I have made extensive use here.

A colloidal mixture is a liquid mixture of two or more substances which are neither separated by the long continued action of gravity nor by passage through filter-paper, although they are separated by the passage through animal membranes or close grained porcelain.

Colloidal solutions.—These as a rule are more or less viscous, gelatinize upon evaporation and go into solution again on the addition of water. They are not coagulated by the addition of small amounts of salts, and, in common with colloidal suspensions, influence the vapor-pressure, freezing-point, boiling-point of the solvent very much less than a corresponding amount of a crystalloid. This is also true for the osmotic pressure of the solution formed. It is evident, then, employing the above definitions of molecular weight in solution, that either their molecular weights are very high, or the definitions do not hold in such cases. At present the question is still open, although from the enormous results obtained for the molecular weights, it would seem that the latter conclusion is the correct one. The osmotic pressure of a 6% glue solution has been found to be but a third of an atmosphere; and the rate of diffusion is also found to be much smaller than for crystalloids.

The colloids of this group include gelatine, agar-agar, unheated albumen, caramel, starch, dextrine, etc. Gelatinized colloids have been found to be permeable to salts in solution, and to offer but an exceedingly slight hindrance to their passage. The electrical conductivity, as a result of this, of salt solutions is observed to be but a few per cent different from the value found in pure water, a fact of which we shall take advantage in Chapter IX. These colloids seem to be impermeable to one another, however.

Colloidal suspensions.—These, in contrast to the other class, are coagulated by the presence of even a small quantity of an electrolyte. They do not gelatinize, as do the others, on cooling, and if gelatinized do not redissolve on heating. The presence of a gelatinizing colloid in even a small quantity prevents the coagulation of colloidal suspensions by salts. Thus, in the presence of gelatine silver chloride precipitated in solution remains in a state of colloidal suspension, and this fact has long been turned to account in the preparing of emulsions in photographic work. It is true, however, that a few other substances serve this same purpose, as sugar, glycerol and even ether.

These suspensions are not only coagulated by the presence of electrolytes, but are not affected at all by the presence of non-electrolytes. Thus the addition of hydrogen sulphide water to a solution of mercuric cyanide produces a colloidal suspension, for neither the hydrocyanic acid formed, nor the other two substances are ionized beyond a slight extent, i.e., all show a small value for

$\alpha = \frac{\mu_v}{\mu_\infty}$. It seems to be necessary to always exceed a certain small minimum quantity of the electrolyte in order to produce coagulation.

Metallic colloidal suspensions may be made (Bredig) by producing an arc under pure water, using electrodes of the metal in question. Some colloidal solutions can be proven to consist of small particles by examination under the microscope, although the number is not very large. One unfailing property of all colloidal mixtures is that they revolve the plane of polarized light, and, in fact, in general behave as though they are made up of exceedingly small particles, although it is impossible to prove that this is always the case.

The effect of the electric current upon colloidal mixtures is exceedingly important, for it gives us some insight into their constitution. Certain suspensions are always carried in the direction of the current through the solution, i.e., coagulate around the cathode (ferric hydroxide). Others, and this is by far the larger class, collect around the anode, i.e., go with the negative current. Of the first group we know of the basic hydroxides (Al, Cr, etc.) and certain dyestuffs. All the rest, the ordinary suspensions as well as the colloids, go in the direction of the negative current and coagulate around the anode.

When a colloid is mixed with another having a different sign, i.e., when two colloids, which go in opposite directions under the influence of the current, are mixed we observe a coagulation, leaving clear solvent above. This is the case with ferric hydroxide (+) and arsenious sulphide (−). Non-electrolytes have no effect upon colloidal mixtures, but electrolytes (above a certain minimum concentration) cause a coagulation, and this effect is apparently proportional to the valence of the ion of the opposite sign to the colloid in question. Since the valence determines the amount of electricity carried by ionized matter, it seems but a natural consequence of our conclusions above, that ionized matter, and that only, outside of the current, can cause the coagulation of these mixtures. From the relation with regard to the migration of colloids with the electric current it is evident that the colloidal particles carry charges of electricity, some always of one sign, some of the other, depending upon their nature. And, further, since non-electrolytes fail to act as do electrolytes, with regard to coagulation, these facts seem to confirm our conclusions that the constituents of electrolytes are charged with electricity. It is assumed that the colloidal particles are charged with one kind of electricity while the liquid in which they exist has the opposite charge. Anything which can disturb this apparent electrical equilibrium, then, and the disturbance apparently must be electrical itself, causes the colloidal mixture to coagulate.

As to how the particles and solvent become differently charged we have only hypothesis as yet, or rather hypotheses, for there are several, and nothing definite is known.

For the latest information as to the size of the particle, etc., as measured by the ultra-microscope, see Svedberg, Z. f. Elektrochem., 12, 853–860, 1906; Zsigmondy, *ibid.* 12, 631–635; and Z. f. phys. Chem., 56, 65–83, 1906; and Biltz, *ibid.* 58, 288–292, 1907.

47. The molecular weight in solution.—Our definitions of molecular weight in solution (osmotic pressure, vapor-pressure, freezing-point and boiling-point) in general lead us to the same results when it is possible to equalize the experimental error and employ all methods. We have found, however, that in some cases the molecular weight so determined is very much smaller than the formula weight (dissociation), and in other cases several times larger than the formula weight (association). Further, two associated liquids (according to definition by surface-tension) when mixed often show a mutual dissociation of the associated state. But these cases, excepting the last, are also found in connection with the molecular weight in the gaseous gas, as it is affected by temperature changes, etc. It is not a question here of any difficulty with our definition of molecular weight, for the various methods seem to agree very well, and it is generally conceded that the various results express

olecular weight as it changes from solvent to solvent,
the same solvent from dilution to dilution.

tain results are found by the freezing-point method
th electrolytes and non-electrolytes, however, which
ard to follow so accurately by other methods, that
ifficult to explain other than by assuming that there
a hydration of the substance in solution. The
ng-point depression, in other words, is found to be
er than it should be from results calculated from
for more dilute solutions. The effect of this hydra-
ould be small as to the increase in the molecular
t due to the addition of water; it is the solvent
is removed which would exert the greater influence
the result, especially on the small amount present
ncentrated solutions. By plotting actually observed
s and assuming water to be removed from the sol-
and to unite with the substance, a curve can be
which will be in accord with the law. In this way
roven that *if* a hydrate were formed to the requi-
xtent, the law would be followed. Later we shall
ler this further (Chap. VIII). Outside of the one
imental fact (see Chap. IX) observed by Morgan
Kanolt (J. Am. Chem. Soc., 26, 635, 1904) the for-
n of compounds of the solute and solvent has not
actually observed. According to the freezing-point
od this hydration has been assumed to take place
both the ionized and the un-ionized portion; the

experimental proof just mentioned refers only to the ionized matter in a solution of silver nitrate in a mixture of water and pyridine.

All the methods given above seem to give explicable results for very dilute solutions; the difficulties will be discussed later. For concentrated solutions, however, it is quite evident that the correct relations have not been obtained as yet. Whether the behavior of very concentrated solutions can ever be brought into accord with the more dilute ones is a question which is still open. It is obvious, though, notwithstanding the difficulties which have arisen, that the theory of solution is a law of nature holding between certain limits, and that the problems in this connection for the future have all to do with enlarging these limits. That this can only be done by following the results closely and avoiding all hypotheses is an opinion which is growing not alone in this branch of science, but in all others. To do this, however, it is not necessary to cast aside what we have learned, thinking it hypothesis, but to use the fragment of a great law of nature which we undoubtedly have in the theory of solution as a basis for further development.

CHAPTER VII.

THERMOCHEMISTRY.

48. Definition.—*Thermochemistry is the subject which treats of the connection between chemical and thermal processes.*

Since almost every chemical process is accompanied by temperature changes, and is more or less influenced by them, this subject is one of great importance.

If a substance is changed from one state into another in such a way that all difference in energy appears in one form, as heat, for example, then this amount, when determined, is proportional to the difference of chemical energy in the two states.

49. Applications of the principle of the conservation of energy.—Hess was the first to apply this principle to thermochemistry. In 1840 he announced the law that *the amount of heat generated by a chemical reaction is the same whether it takes place all at once or in steps.* In other words, *all transformations from the same original state to the same final state liberate the same amount of heat, irrespective of the process by which the final state* *is reached.* The heat liberated in a reaction, then, depends only upon the final and initial states. This was entirely the result of experiment on the part of Hess, who did not consider it, as we do to-day, as self-evident. The truth of this principle he showed by the equality in the heat of formation of ammonium chloride in water when prepared in two dissimilar ways; for he found by experiment that

$$\text{gas}\cdot NH_3+\text{gas}\cdot HCl=\text{solid } NH_4Cl+42100 \text{ cal.}$$

and

$$\text{solid } NH_4Cl+\text{water}=NH_4Cl \text{ in solution}-3900 \text{ cal.,}$$

so that

$$\text{gas}\cdot NH_3+\text{gas}\cdot HCl+\text{water}=NH_4Cl \text{ in solution}+38200 \text{ cal.;}$$

while from

$$\text{gas}\cdot NH_3+\text{water}=NH_3 \text{ in solution}+8400 \text{ cal.}$$
$$\text{gas}\cdot HCl+\text{water}=HCl \text{ in solution}+17300 \text{ cal.}$$

and

$$NH_3 \text{ in solution}+HCl \text{ in solution}=NH_4Cl \text{ in solution}+12300 \text{ cal.}$$

it is evident that

$$\text{gas}\cdot NH_3+\text{gas } HCl+\text{water}=NH_4Cl \text{ in solution}+38000 \text{ cal.}$$

Upon this law the whole subject of thermochemistry is based, for by it it is possible to find indirectly the heat liberated or absorbed by any reaction. *This is true, even though it is not possible to carry out the reaction in practice. We have simply to consider the process as a part or a sum of others which have been measured; then,* *by the addition of the equations, all undesired substances may be caused to disappear until finally the desired reaction is found.*

The chemical symbols, as we have used them up to now, have represented only the molecular weights of the substances in question. Now, however, when we are considering as well the quantity of energy absorbed or liberated by the reaction, the symbols have a further meaning which must not be overlooked. In addition to the weight in grams expressed by the formula weights of the substances, the symbols also represent the amount of energy contained in that weight in this state as compared to the energy contained in another, the standard, state. Thus the equation

$$\mathbf{C}+2O=CO_2+97000 \text{ cals.}$$

means that the energy contained in 12 grams of solid carbon and 32 grams of gaseous oxygen is greater by 97000 cals. than that contained at the same temperature in 44 grams of gaseous carbon dioxide.

The small calorie, cal., as will be seen, is so small that the numbers employed are very large, and, more important still, do not express well the experimental limitations of the determination. For this reason the Ostwald calorie (K) is much better adapted for the purpose. This is the heat which is necessary to raise the temperature of 1 cc. of H_2O from 0° to 100° C., and is related to the large and small calories in approximately the following way:

$$K = 100 \text{ cals. (i.e., 1 cc. } H_2O \text{ 1° C.);}$$
$$10K = 1 \text{ Cal. (i.e., 1 kg. of } H_2O \text{ 1° C.).}$$

It will be observed here that one unit in terms of the Ostwald calorie expresses about the limit of accuracy of experimental observations, while of the other two, one leads to the impression that the experimental result is more accurate than it is, the other that it is less accurate.

In addition to these units we also have others which are still more convenient, for they are based upon the erg. The joule, designated by j, is equal to 10^7 ergs, and a unit one thousand times this, i.e., 10^{10} ergs is designated by J. We have, then,

$$1 \text{ cal.} = 4.183 \text{ j and } 1 \text{ j} = 0.2391 \text{ cal.} = 10^7 \text{ ergs,}$$

or

$$1 \text{ cal.} = 0.004183 \text{ J and } 1 \text{ J} = 239.1 \text{ cal.} = 10^{10} \text{ ergs.}$$

In all reactions we shall distinguish the state of aggregation according to the system proposed by Ostwald, in which ordinary letters are used for liquids, heavy ones for solids, and italics for gases.

In considering substances in solution it is necessary to know the heat which is liberated by this process. This is called the *heat of solution.* For different amounts of water, of course, this will vary, so that for uniformity the heat of solution is always understood to be the heat (positive or negative) which is liberated by the solution of 1 mole in so much water that an addition of more water will give no additional heat effect. This is designated by the addition of the abbreviation Aq (aqua) to the symbol of the substance, and is what was designated as "water" in the equations of Hess above. It is always to be remembered, however, that an isolated Aq in an equation is not equal to an H_2O, which refers to 18 grams of water, although a mole of water may be considered as abstracted from the term Aq, as in the reaction above,

$$NH_3+\mathrm{Aq}=\mathrm{NH_4OHAq}+8400 \text{ cal.}$$

The following example of the determination, by the process of elimination, of the heat liberated by a reaction will probably make the method clear. Calculate the heat evolved by the reaction

$$\mathrm{MgCl_2}+2\mathrm{Na}=2\mathrm{NaCl}+\mathrm{Mg},$$

when the following experimental data are known:

$(-2)\ \mathrm{NaCl}+\mathrm{Aq}=\mathrm{NaClAq}-11.8K;$

$(-1)\ 2H_2+O_2=2\mathrm{H_2O}+1368K;$

$(+1)\ 2\mathrm{Na}+O_2+H_2+\mathrm{Aq}=2\mathrm{NaOHAq}+2236K;$

$(+2)\ \mathrm{NaOHAq}+\mathrm{HClAq}=\mathrm{NaClAq}+\mathrm{H_2O}+137K;$

$(-1)\ \mathrm{Mg}+2\mathrm{HClAq}=\mathrm{MgCl_2Aq}+H_2+1083K;$

$(+1)\ \mathrm{MgCl_2}+\mathrm{Aq}=\mathrm{MgCl_2Aq}+359K.$

By adding these equations, after multiplying each of the factor in the parenthesis, we find

$$MgCl_2+2Na=2NaCl+Mg+441.6K.$$

In the same way we can find the heat of combustion of carbon in oxygen, a value which cannot be directly measured. Two reactions which have been measured are

$$C+2O=CO_2+970K$$

and

$$CO+O=CO_2+680K(-).$$

Adding these, after changing the signs of the second, we obtain

$$C+\ O=CO+290K,$$

i.e., the sum of the energies contained in 12 grams of solid carbon and 16 grams of gaseous oxygen is 290*K* greater than that contained in 28 grams of gaseous carbon monoxide.

The process consists, then, in combining a number of measured reactions in such a way that the final one is obtained.

50. The heat of formation.—If the heats of formation of the substances from their elements are known, then it is simpler to substitute these in a reaction and solve for the unknown term. This saves the trouble of eliminating from a large number of equations.

If in a reaction we imagine all substances to be decomposed into their elements before the reaction begins, then the final result of the reaction, after both sides are in the final state, will naturally be the difference in the sums of the heats of formation on the two sides. We have, then, the rule: *To find the heat liberated by a reaction it is simply necessary to subtract the sum of the heats of formation of the original substances from that of those of the final substances, the heat of formation of elements being counted as zero.*

Since, in the reaction,

$$\mathbf{Pb} + 2I = \mathbf{PbI_2} + 398K,$$

$$0 = \mathbf{PbI_2} + 398K,$$

or

$$\mathbf{PbI_2} = -398K,$$

we can substitute for the chemical symbols in an equation the negative values of the heats of formation and solve for the unknown term.

Examples.—Find the change in heat energy caused by the decomposition of $\mathbf{MgCl_2}$ by $\mathbf{Na}$. We have

$$\mathbf{MgCl_2} + 2\mathbf{Na} = 2\mathbf{NaCl} + \mathbf{Mg} + xK.$$

The heat of formation of $MgCl_2 = 1510K$, and that of $2NaCl = 1951.6K$; hence

$$-1510 = -1951.6 + x;$$

$$x = 441.6K.$$

What is the heat of formation of $KMnO_4$? We have the reaction

$$2KMnO_4Aq + 5SnCl_2HClAq = 5SnCl_4Aq + 2KClAq$$
$$+ 2MnCl_2Aq + 8H_2O + 3867K,$$

or, substituting the negative values of the heats of formation,

$$-2x - 4057 - 6290 = -7859 - 2023 - 2500 - 5469 + 3867;$$

hence

$$x = 1818K.$$

To obtain this result by the method of elimination would require about twenty equations, which in a direct elimination would cause considerable confusion.

This substitution method, when it can be used, is much less confusing than the one based upon elimination, for by use of it, at worst, i.e., when the heats of formation have not been directly determined, we can break up the one, general, elimination into as many separate eliminations as there are separate compounds in the reaction. This fact is shown very clearly by a comparison of the two methods as applied to the reaction between solid $MgCl_2$ and solid NaCl. Knowing, in addition to the six equations given for the elimination, that

$$H_2+Cl_2+\mathrm{Aq}=2\mathrm{HClAq}+786K,$$

it is possible to break up the one, general, elimination into two separate ones, i.e., one for the heat of formation of solid $MgCl_2$, the other for solid NaCl. These two values can then be substituted in the original equation, just as though they had been found directly and the result obtained without the possibility of confusion which might otherwise be present.

The heat of formation of organic compounds can be found from the heats of combustion in oxygen. If the elements remain behind in the uncombined state the negative value of the one would give the other. The elements, however, unite to form H_2O, CO_2, etc., so that the heats of formation of these must be subtracted from the heat measured to obtain the true value of the formation from the elements.

In order to save time heats of formation, instead of being given in full, as

$$H_2+Cl_2+\mathrm{Aq}=2\mathrm{HClAq}+786K,$$

are often written in the form

$$(H_2,\ Cl_2,\ \mathrm{Aq})=786K;$$

i.e., only the substances on the left of the chemical equation are given, and are separated by commas and inclosed in a parenthesis.

51. Chemical changes at a constant volume.—When the volume of a chemical reaction is held constant, or *when the external work (positive or negative) involved in the change in volume is not included in the heat of the reaction*, the reaction is said to take place at constant volume. In other words, the condition of constant volume means the condition involving no positive or negative external work to the system. Under such conditions *the energy in one state is then equal to that in the other plus the amount of heat generated by the change*. The chemical symbols which we use in such cases express, in addition to the ordinary chemical meaning, *the energy contained in one mole.*

52. Chemical changes at a constant pressure.—If the volume changes during the reaction, and the system loses heat equivalent to the work of expansion, or gains heat equivalent to the work done upon it by a compression, the reaction is said to take place at *constant pressure*. The only difference between constant volume and constant pressure conditions, then, is that no matter how the volume may change, the heat equivalent to the work of the change is not considered as affecting the energy of the system under constant volume conditions, while it is considered as a loss (expansion) or a gain (comession) to the system when under constant pressure nditions.

This loss or gain may be neglected in all cases where gas is formed, simply because the correction is very all as compared to the heat of the reaction. Thus, r example, we will calculate the correction to be used an increase of volume equal to 1 cc. Here $dv=1$ d $p=1033$ grams and the work, $pdv=1033$ gr.-cms., ich is equal to

$$\frac{1033}{42600}=0.024+\text{ cal. or }0.00024K.$$

f 1 mole of base is mixed with 1 mole of acid $137K$ generated, and the volume increase is equal to 20 cc. nce the correction to be applied here is

$$20\times 0.00024K=0.0048K,$$

ich is so small compared to $137K$ that it may be glected.

When a gas is formed the increase of volume may ecome very large; consequently it is necessary in such ases to use the correction. By definition the external work done by the formation at T° of 1 mole of gas from negligible volume is $2T$ cal., or $0.02TK$, and for n moles is $0.02nTK$, hence, *in any reaction, for each mole of gas formed, at the absolute temperature T under constant pressure, the energy of the substance is decreased by* $0.02TK$.

In the case of the absorption of the gas the energy is increased by this amount.

Thus if 1 mole of gas is formed by a reaction at 18° C. the amount of heat used for its formation is

$$0.02 \times (273^\circ + 18) = 5.82K.$$

And at any one temperature this is independent of the pressure p.

Under constant pressure, the symbols, in addition to the chemical significance, represent the energy *plus the term* pv *for 1 mole.* This term pV may be either positive or negative, according as the gas is absorbed or formed.

53. Relation between results for constant volume and constant pressure.—Since what we call the constant volume condition is a no-external-work condition, whether the volume really remains constant or not, and a constant pressure condition is an external-work condition, no matter how the pressure varies so long as the volume changes; and external work done means a loss of heat, and work done upon the system means a gain of heat, it is evident that the relation between the heat energy of a reaction at constant volume and that at constant pressure can be represented by the equation

$$Q_p = Q_v - n(0.02TK),$$

where *n* is the number of moles of gas *formed* in excess of those originally present, and consequently is negative when gas, in place of being formed, is absorbed by the reaction.

In this way it is possible to make all our determinations for constant volume and then calculate the result to constant pressure. This latter is the more useful term, for all our reactions take place in that way under atmospheric pressure. The former, however, is that usually determined in the bomb-calorimeter. An example of the calculation from one condition to the other is given below. Find from the reaction

$$H_2 + O = \mathrm{H_2O} + 674.84K \text{ at } 18° \text{ const. vol.},$$

the heat generated if the reaction takes place under a constant pressure. By the reaction 1 mole of hydrogen disappears with 1/2 of a mole of oxygen and forms 1 mole of liquid water (no gas); consequently the heat under constant pressure will be larger than that for constant volume by the amount $1\frac{1}{2} \times 0.02TK$, for $n = -1\frac{1}{2}$. We have, then,

$$674.84 + 1\tfrac{1}{2} \times 0.02 \times 291 = 683.57K = Q_p,$$

as the value for constant pressure at 18° C.

54. Effect of temperature.—If we allow a reaction to take place first at the temperature t_1 and then at the temperature t_2 the amounts of heat evolved are found to be different; assume them to be Q_1 and Q_2 respectively.

Starting with the constituents, imagine the reaction taking place at the temperature t_1, at which the amount of heat Q_1 is evolved, and then heated to the temperature t_2. If c' is the total heat capacity of the resulting products the amount of heat necessary for this rise in temperature is $c'(t_2-t_1)$. The reaction has now taken place and the temperature is t_2.

Starting again with the constituents at the temperature t_1 assume them to be heated to t_2 and then to react, evolving the heat Q_2. The heat necessary for this rise in temperature is $c(t_2-t_1)$, where c is the total heat capacity of the original substances.

We have started, thus, with the same original substances at the same temperature and obtained the same products, at the same final temperature; hence, by the law of the conservation of energy (pp. 41–42) the amounts of heat involved must be the same. We have, then,

$$Q_1-c'(t_2-t_1)=Q_2-c(t_2-t_1),$$

i.e.,

$$Q_2-Q_1=(c-c')(t_2-t_1),$$

$$\frac{Q_2-Q_1}{t_2-t_1}=c_{\text{orig.}}-c_{\text{final}},$$

or, for small changes,

$$\frac{\Delta Q}{\Delta t}=c_{\text{orig.}}-c_{\text{final}}.$$

The change in the heat of reaction per degree of temperature is equal to the amount of heat necessary to raise the temperature of the total weight of the left side of the chemical equation 1°, *minus that necessary to raise the total weight of the right side* 1°. It will be observed, then, that the only change in the heat of reaction with the temperature is that due to the specific heat of the substances present.

It is to be noted here that if c_{final} is larger than $c_{\text{orig.}}$ the sign of $\frac{\Delta Q}{\Delta t}$ will be negative. This indicates that an increase of temperature gives a decrease in the heat of the reaction, i.e., the heat varies inversely with the temperature. If c_{final} is smaller than c_{orig} the term $\frac{\Delta Q}{\Delta t}$ is positive and Q varies directly as the temperature.

Example.—When 4 grams of hydrogen at 18° combine with 32 grams of oxygen at the same temperature to produce 36 grams of liquid water, 1367.1K are evolved.

How much heat will be evolved if the same masses of hydrogen and oxygen combine at the temperature of 200° and the product of the combination is maintained at this temperature, the pressure being constant? The specific heats per gram are: 3.409 for H, 0.2175 for O, 1 for H_2O from 18° to 100°, and 0.4805 for H_2O between 100° to 200°. The latent heat of evaporation of water is 536.5, all values being expressed in small calories.

For liquid water up to 100° we have the relation

$$(4\times 3.409+32\times 0.2175)-(36\times 1)=\frac{\Delta Q}{\Delta t}=-15.404 \text{ cals.},$$

and since this is for 1°, we have for 82° (i.e., 100−18) $82\times(-15.404)=1263$ cals. The heat of formation of liquid water at 100°, then, is

$$1367.1-12.63=1354.47K.$$

But in going into water-vapor at 100° 36×536.5 cals. of this is absorbed by the system, i.e., hydrogen and oxygen forming gaseous water at 100° evolves

$$1354.47-193.14=1161.33K.$$

For the reaction between 100° and 200° for gaseous water, as formed from gaseous hydrogen and oxygen, we have the temperature coefficient

$$(4\times 3.409+32\times 0.2175)-(36\times 0.4805)=\frac{\Delta Q}{\Delta t}=2.3 \text{ cals.},$$

and, for the interval of 100° (i.e., 200 − 100),

$$100\times 2.3=230 \text{ cals.}=2.3K.$$

In total, then, we have

$$1161.33+2.3=1163.63K$$

as the heat of transformation according to the reaction

$$\underbrace{2H_2+O_2}_{18^\circ}=\underset{200^\circ}{2H_2O}.$$

55. The thermal reactions of electrolytes.—*Two salt solutions which are so dilute that the ratio* $\frac{\mu_v}{\mu_\infty}$ (p. 190) *is equal to 1, do not evolve or absorb heat when mixed, provided no chemical reaction takes place between them.*

This fact was first observed by Hess and has been confirmed by all observers since.

Another experimental fact observed to hold for solutions of electrolytes is as follows: *When an acid is neutralized by a base, both being in so great a dilution that the value* $\frac{\mu_v}{\mu_\infty}$ *for each is equal to 1, as is also that of the salt formed, the heat evolved is equal to 137K and is independent of the nature of the base and acid used* *or the salt formed, so long as this latter at that diluti fulfills the condition* $\frac{\mu_v}{\mu_\infty}=1$.

These facts, taken in connection with those mentione above (pp. 180–200) and the conclusions arrived at ther are not so startling as one might imagine at first glanc Since for the acid and base we have the relation

$$\mu_{\infty\,\mathrm{acid}}+\mu_{\infty\,\mathrm{base}}-\mathrm{const.}=\mu_{\infty\,\mathrm{salt}},$$

the constant being independent of the nature of eithe the acid, the base, or the salt, and, since the salt i observed to have a molecular weight (by definitio equal to one-half the formula weight, i.e., is completel ionized according to all the possible methods of measurement, it is quite certain that it is made up of the substances previously composing the acid and base in th same state as that in which they existed in them. I other words, expressing the chemical equation in accor with the experimental facts above, we have

$$\mathrm{H}^{\cdot}+\mathrm{A}'+\mathrm{M}^{\cdot}+\mathrm{OH}'+n\mathrm{H_2O}=\mathrm{A}'+\mathrm{M}^{\cdot}+(n+1)\mathrm{H_2O},$$

where n represents the number of moles of water present in the system before the reaction.

Since the conductivity shows the constituents of the salt (the ions) to be present in the same form they were in originally, the only portion of the reaction which could possibly involve heat is the formation of water from ionized hydrogen ($H^{\cdot}$) and ionized hydroxyl (OH'). As we know that hydrogen and hydroxyl in the ionized state can exist together to but an infinitesimal extent (for pure water conducts only very slightly), the following conclusion is certainly justified. When an acid unites with a base (at any rate in the condition in which we have assumed them) the cause of the reaction is the inability of ionized hydrogen to exist in the presence of ionized hydroxyl beyond an exceedingly small amount; and the heat of the neutralization (for this case) is that heat which is evolved during the formation of *water from its ions* in this way, i.e., $137K$ for each mole of $H^{\cdot}$ and OH' (by definition) forming one mole of H_2O at 25°.

By a method which we shall consider later (Chap. VIII) it is possible not only to show the presence of, but to calculate accurately, the heat involved in the dissociation of a substance. When the acid and salt are completely ionized, for example, and the base but slightly, it is possible to show just how much extra heat (either positive or negative) is involved by the further dissociation of the base. For the partly dissociated base must increase in dissociation as its ionized OH is used up, since the more dilute the solution of the base the greater is its ionization, up to a certain point.

If both the acid and base are but partly dissociated the result will differ still more, for heat will be absorbed or evolved by the further dissociation of both of these. And if the salt, also, is not completely dissociated, i.e., if more heat is liberated by its undissociated product being formed, we shall have a still further quantity.

It is evident, then, that *the heat generated by the neutralization of an acid by a base is equal, for each mole of water formed, to 137K plus the heat produced by the amount of un-ionized salt formed, plus the sum of the heats evolved in the completion of the ionizations of the acid and the base.*

It is for this reason that we get a larger heat of neutralization for certain acids with caustic soda than for others, for heat is given out by the further ionization of the acid and association of the salt; *and consequently the heat of neutralization is in no sense a criterion as to the strength of the acid.*

Later we shall consider this relation more in deatil, i.e., after we have studied the method to be used for the calculation of the heat of dissociation.

It is obvious from the above that the thermal properties of electrolytes are additive when they are in such a dilution that they fulfill the condition $\frac{\mu_v}{\mu_\infty} = 1$. When not in this condition the change in the thermal effect depends upon the amount of heat involved in causing them to alter their states.

When a precipitate is formed in such a solution (i.e., when a chemical reaction takes place, which was excluded above) it is often possible to find its heat of formation just as we found that of water. An example of this is the following:

$$\mathrm{Ag^{\cdot}Aq + NO'_3Aq + Na^{\cdot}Aq + Cl'Aq = AgClAq + Na^{\cdot}Aq} \\ \mathrm{+ NO'_3Aq} + 158K$$

or

$$\mathrm{Ag^{\cdot}Aq + Cl'Aq = AgClAq} + 158K$$

i.e., when 1 mole of AgCl is formed from the ionized silver and ionized chlorine in a solution heat equal to $158K$ is evolved. Conversely if 1 mole of AgCl were dissolved, this amount of heat would be absorbed, i.e., the heat of solution of a substance is equal to the negative value of the heat of precipitation.

Although this is not always possible, we can find the heat of formation in solution in another way. The principle of this is as follows: By electrical measurements it has been possible to find the amount of heat involved when 2 grams of gaseous hydrogen form 2 grams of ionized hydrogen in solution. This value is approximately equal to 4 J, but since there is some uncertainty about its exact value, it is usual to assume it equal to zero. Later, then, the results based upon this can be readily recalculated. From this value, by dissolving a metal in a completely ionized acid, i.e., by the substitution of metal in the ionized state for the hydrogen, which is evolved as a gas from that state, we can observe directly the heat of formation of the ionized metal from massive metal. By then determining the heat of solution of a completely ionized salt of this metal, the heat due to the negative radical can be determined readily, for the heat of solution of the salt is equal to the sum of the heats of ionization of the constituents, of which we assume that of hydrogen to be zero.

Cathions		J = joules × 10³
Hydrogen	$H^{\cdot}$	+ 0
Potassium	$K^{\cdot}$	+259
Sodium	$Na^{\cdot}$	+240
Lithium	$Li^{\cdot}$	+263
Rubidium	$Rb^{\cdot}$	+262
Ammonium	$NH_4^{\cdot}$	+137
Hydroxylamine	$NH_4O^{\cdot}$	+157
Magnesium	$Mg^{\cdot\cdot}$	+456
Calcium	$Ca^{\cdot\cdot}$	+458(?)
Strontium	$Sr^{\cdot\cdot}$	+501
Aluminium	$Al^{\cdot\cdot\cdot}$	+506
Manganese	$Mn^{\cdot\cdot}$	+210
Iron	$Fe^{\cdot\cdot}$	+ 93
	$Fe^{\cdot\cdot\cdot}$	− 39
Cobalt	$Co^{\cdot\cdot}$	+ 71
Nickel	$Ni^{\cdot\cdot}$	+ 67
Zinc	$Zn^{\cdot\cdot}$	+147
Cadmium	$Cd^{\cdot\cdot}$	+ 77
Copper	$Cu^{\cdot\cdot}$	− 66
	$Cu^{\cdot}$	− 67(?)
Mercury	$Hg^{\cdot}$	− 85
Silver	$Ag^{\cdot}$	−106
Thallium	$Tl^{\cdot}$	+ 7
Lead	$Pb^{\cdot\cdot}$	+ 2
Tin	$Sn^{\cdot\cdot\cdot}$	+ 14

Anions of		J = joules × 10³
Hydrochloric acid	Cl'	+ 164
Hypochlorous acid	ClO'	+ 109
Chloric acid	ClO_3'	+ 98
Perchloric acid	ClO_4'	− 162
Hydrobromic	Br'	+ 118
Bromic acid	BrO_3'	+ 47
Hydriodic acid	I'	+ 55
Iodic acid	IO_3'	+ 234
Periodic acid	IO_4'	+ 195
Hydrosulphuric acid	S''	− 53
	HS'	+ 5
Thiosulphuric acid	S_2O_3''	+ 581
Dithionic acid	S_2O_6''	+1166
Tetrathionic acid	S_4O_6''	+1093
Sulphurous acid	SO_3''	+ 633
Sulphuric acid	SO_4''	+ 897
Hydrogen selenide	Se''	− 149
Selenious acid	SeO_3''	+ 501
Selenic acid	SeO_4''	+ 607
Hydrogen telluride	Te''	− 146
Tellurous acid	TeO_3''	+ 323
Telluric acid	TeO_4''	+ 412
Nitrous acid	NO_2'	+ 113
Nitric acid	NO_3'	+ 205
Phosphorous acid	HPO_3'	+ 603
Phosphoric acid	PO_4'''	+1246
	HPO_4''	+1277
Arsenic acid	AsO_4'''	+ 900
Hydroxyl	OH'	+ 228
Carbonic acid	HCO_3'	+ 683
	CO_3''	+ 674

In this way the table given on p. 234 has been prepared by Ostwald. In order to find the heat of formation of the salt it is only necessary to form the sum of the heats due to the ions into which it decomposes, taking into account the valence of the ions as indicated by the dots for the electro-positive and the accents for the electro-negative substances.

These numbers hold only for the case that the substances are in very dilute solution, i.e., Aq should be added to the symbol of each ion. For stronger solutions, in which the ionization is not complete, other amounts of heat are involved which, unless allowed for, will lead to incorrect results.

The equations

$$Na = Na^{\cdot} + 240\ J$$

and

$$Cl_2 = 2Cl' + 2 \times 164\ J$$

mean that by the transformation of the formula weight of metallic sodium into the ionized state 240 J are evolved; and for the change of the formula weight of chlorine gas into two formula weights of ionized chlorine (p. 189) 2 × 164 J are liberated.

CHAPTER VIII.

CHEMICAL CHANGE.

A. EQUILIBRIUM.

56. Reversible reactions.—If we bring a number of reacting substances together in a chemical system, and leave them for a sufficient length of time, the reaction will reach an end, and we shall have, according to a previous general definition, a solution, i.e., a mixture containing solids, gases, or liquids, or all three.

To represent any chemical reaction we may use the equation

$$n_1A_1+n_2A_2+n_3A_3+\ldots=n_1'A_1'+n_2'A_2'+n_3'A_3'+\ldots$$

Here n_1 moles of A_1, n_2 of A_2, n_3 of A_3, etc., unite to form n_1' moles of A_1', n_2' of A_2', n_3' of A_3', etc. When all these substances can remain together for an indefinite length of time, without the reaction going in either direction to produce a lasting change, they are said to exist in chemical equilibrium.

Reactions which go partly from left to right when we start with the substances A_1, A_2, etc., and partly from right to left when we start with A_1' A_2', etc., are called *reversible or reciprocal reactions, provided that in each* *case, starting with equivalent amounts, the final equilibrium is the same for both directions.*

An excellent example of such a reaction is

$$\underset{\text{Alcohol.}}{C_2H_5OH} + \underset{\text{Acetic Acid.}}{CH_3COOH} \rightleftarrows \underset{\text{Ethyl Acetate.}}{CH_3COOC_2H_5} + \underset{\text{Water.}}{H_2O}.$$

If we start from the left side we obtain a certain definite amount of those on right and *vice versa*. For example, 1 mole (46 grams) of alcohol plus 1 mole (60 grams) of acetic acid, or 1 mole (88 grams) of ethyl acetate plus 1 mole (18 grams) of water, will always give the same final state, in which we have

$$1/3 \text{ mole alcohol} + 1/3 \text{ mole acetic acid} + 2/3 \text{ mole ethyl acetate} + 2/3 \text{ mole water.}$$

57. The law of mass action.—Considering such a reversible reaction as that above, or, for example,

$$2HI = H_2 + I_2,$$

the question at once arises—in which direction and to what extent will such a reaction go when we start, for instance, with a certain concentration or pressure of each of the three gaseous constituents, HI, I and H?

From the purely chemical point of view the above equation simply provides that *if* we start with 1 mole of hydrogen and 1 mole of iodine, and *if* these unite completely, 2 moles of hydriodic acid gas will be formed; or *if* we start with 2 moles of hydriodic acid gas, and this is completely decomposed we shall obtain 1 mole each of hydrogen and iodine. As to what portion of the hydrogen and iodine will unite to form hydriodic acid; or what portion of the total original amount of hydriodic acid will decompose to form hydrogen and iodine; or what will take place if all three are mixed together; we are utterly ignorant, failing further information than that contained in the chemical equation.

The answers to these questions can only be obtained by the application of a very general law which was first announced by Guldberg and Waage in 1864. The qualitative form of this *law of mass action* is as follows: *Chemical action, at any stage of the process, is proportional to the active masses of the substances present at that time, i.e., to the amounts of each present in the unit of volume.*

In this form, however, the law of mass action is of but little practical use. It will be necessary, then, for us to derive a quantitative expression of it, and thus to obtain it in such a form that it may be applied to our needs in answering questions such as those alluded to above.

Imagine a reaction of the type

$$n_1A_1+n_2A_2 \rightleftarrows n_1'A_1'+n_2'A_2'$$

having taken place in a closed vessel and to have attained a state of equilibrium in which we have the partial pressures p_1, p_2, p_1' and p_2'.

Assume, further, that it is possible to insert each of the substances on the left against its gaseous or osmotic pressure p_1, p_2, and to remove each of the products, as they are formed, from the gaseous or osmotic pressure p_1', p_2' to the original external pressure p_0—and that this insertion and removal is isothermal and reversible.

Since by such a series of operations we would do work on one side $(-)$, and obtain work $(+)$ from the other, the sum of the two amounts (regarding the signs) would give us an expression for the work $(+\text{or}-)$ which is done *by the system itself* during the transformation, at constant temperature, of n_1 moles of A_1 and n_2 moles of A_2 to n_1' moles of A_1' and n_2' moles of A_2', the initial and final pressure being the same, viz., p_0. And this in its turn would lead to the expression of the quantitative relation existing between the active masses of the constituents at equilibrium, i.e., to the relation we seek.

Since the work required to change the osmotic or gaseous pressure of 1 mole of substance from p_0 to p_1 is given by the expression $RT\log_e\frac{p_1}{p_0}$,* that for n_1 moles will be $n_1RT\log_e\frac{p_1}{p_0}$. For n_2 moles of A_2 we have the corresponding expression $n_2RT\log_e\frac{p_2}{p_0}$. The sum of these two terms is the work done, i.e., lost, by us in the process. The gain of work for us then for this stage is

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* Work $= Vdp = \frac{RT}{p}dp = RT\int_{p_0}^{p_1}\frac{dp}{p} = RT\log_e\frac{p_1}{p_0}$. Robertson (J. Phys. Chem., 10, 521–523, 1906) in this connection has pointed out that even if $pV=RT$ does not hold, but $p(V-d)=RT$ does, the derivation will still be correct, for the constant d would disappear.

$$-RT\left(n_1\log_e\frac{p_1}{p_0}+n_2\log_e\frac{p_2}{p_0}\right).$$

By the removal, as they are formed, of n_1' moles of A_1' and n_2' moles of A_2', the amount of work (a gain for us) is

$$RT\left(n_1'\log_e\frac{p_1'}{p_0}+n_2'\log_e\frac{p_2'}{p_0}\right).$$

In total, then, our gain in work in transforming n_1 moles of A_1 and n_2 moles of A_2 into n_1' moles of A_1' and n_2' moles of A_2' at constant temperature, the initial and final pressure being p_0, is

$$W=RT\left(n_1'\log_e\frac{p_1'}{p_0}+n_2'\log_e\frac{p_2'}{p_0}-n_1\log_e\frac{p_1}{p_0}-n_2\log_e\frac{p_2}{p_0}\right),$$

or

$$\begin{aligned}W=&RT(n_1\log_e p_0+n_2\log_e p_0-n_1'\log_e p_0-n_2'\log_e p_0)\\&+RT(n_1'\log_e p_1'+n_2'\log_e p_2'-n_1\log_e p_1-n_2\log_e p_2).\end{aligned}$$

But, as we simply wish to get the relation which depends upon the pressures in the reaction at equilibrium, and the pressure p_0 has nothing to do with this, we can assume p_0 to be 1, and obtain, since the first term is equal to zero,

$$W' = RT(n_1' \log_e p_1' + n_2' \log_e p_2' - n_1 \log_e p_1 - n_2 \log_e p_2).$$

As the processes of insertion and removal are assumed to be isothermal and reversible this work, W', for $p_0 = 1$, must be *the maximum work which can be done by the reaction*, and hence must be a constant at any one temperature.

We have, then,

$$(18) \qquad W' = \text{constant} = RT \log_e \frac{p_1'^{n_1'} \, p_2'^{n_2'}}{p_1^{n_1} p_2^{n_2}},$$

and since if the logarithm is a constant the expression itself must be a constant, and since T and R are also constants,

$$(19) \qquad \text{Constant} = K_p = \frac{p_1'^{n_1'} \, p_2'^{n_2'}}{p_1^{n_1} p_2^{n_2}},$$

or since at any one temperature pressure and concentration are proportional, we have where the relationship between K_p and K_c can be readily found as follows: Since $c = \frac{1}{V} = \frac{p}{RT}$,

$$K_c = \frac{\left(\frac{p_1'}{RT}\right)^{n_1'} \left(\frac{p_2'}{RT}\right)^{n_2'}}{\left(\frac{p_1}{RT}\right)^{n} \left(\frac{p_2}{RT}\right)^{n_2}} = (RT)^{n_1+n_2-n_1'-n_2'} K_p.$$

The constant for concentrations is equal to that for pressures multiplied by RT raised to a power equal to the difference between the number of moles originally present and those finally present in the chemical equation. Calling the initial moles Σn and the final one $\Sigma n'$ we have $K_c = K_p(RT)^{\Sigma n - \Sigma n'}$. When the reaction is similar to $2HI = H_2 + I_2$, i.e., when we have the same number of moles on each side (2), $\Sigma n - \Sigma n'$ becomes zero, and $K_c = K_p$.

The constant (K_p or K_c) is known as the *constant of equilibrium.*

We may express the *law of mass action* as follows, then at equilibrium *the product of the pressures (concentrations) of the substances on the right (final ones), each raised to a power equal to the number of the moles reacting divided by the product of the pressures (concentrations) of the substances on the left (initial ones), each raised to a corresponding power, is a constant for any one reaction at any definite temperature.*

The variation of this constant, K_p or K_c with the temperature is to be considered later, after we have studied the application of this most important and general law.

58. Equilibrium in homogeneous gaseous systems.—For gases we can most conveniently use the form of the law of mass action which refers to partial pressures, (19). We have, then, for the equilibrium of a gaseous chemical system

$$K_p=\frac{p_1'^{n_1'}p_2'^{n_2'}\ldots}{p_1^{n_1}p_2^{n_2}\ldots}.$$

An example of this is given by the gaseous reaction

$$2HI=H_2+I_2.$$

If the partial pressure of H is p_1, that of I p_2, and that of HI p, then

$$K_p=\frac{p_1p_2}{p^2}.$$

This case was investigated by Bodenstein, who found by experiment that at a temperature of boiling sulphur (440°)

$$K_p=0.02012.$$

If we heat hydriodic acid, then, to this temperature, it is possible to calculate from its amount the amounts of hydrogen and iodine and undecomposed hydriodic acid in the gaseous state present at equilibrium.

The total pressure of a mixture of gases is equal to

$$P = p_{HI} + p_I + p_H,$$

where the terms on the right are the partial pressures. If H and I are present in the free state at the partial pressures a and b and HI to d, and we wish to find in what direction and to what extent the reaction will go; we proceed as follows: Let x represent the partial pressure of H lost; then, according to the reaction $2HI = H_2 + I_2$, we shall have, *at equilibrium*, for the partial pressure of HI, *if the volume remains constant*,

$$p_{HI} = d + 2x,$$

for H uncombined

$$p_H = a - x,$$

and for I uncombined

$$p_I = b - x.$$

x must have such a value, then, (i.e., the reaction must go so far) that *at equilibrium* it will just satisfy the equation of the law of mass action, for the reaction at 440°.

$$K_p = 0.02012 = \frac{(a-x)(b-x)}{(d+2x)^2}.$$

Knowing a, b, and d, it is possible to solve the equation for x, and to find how, and how far the reaction will go. For example, in this case, if x is positive in value, the reaction will go toward the left, as we have assumed; if negative, in the opposite direction.

There is one thing to be said of the solution of such equations. There are two possible values of x; which is to be taken? It will be found in this case, as, indeed, in all others, that only one value is in accord with the existing data, so that it alone could be taken. For instance, if the positive value of x is larger than a or b it would lead to an absurdity, for it would show a negative value for H or I, and the other value is the correct one. In cases of equations of a higher degree, where more than two roots exist, this same rule is to be followed. A possible case here is to have two values of the same sign, but one smaller than the other. There can be no question in such a case, however, for if the reaction would be in equilibrium after the smaller change had occurred, it could not go out of this state to attain the equilibrium shown by the greater value, hence the lower value is to be taken as the correct one.

Here we have used the partial pressure form of the law of mass action; we could use the other just as well however, for, as was mentioned above, the constant for this reaction, as for all others with the same number of formula weights on both sides, has the same value for concentrations, pressures, volumes under standard conditions, or any other term proportional to concentrations or pressures.

A further effect of this condition of equal volume on the two sides is that the progress of the reaction is perfectly independent of pressure (Le Chatelier's theorem, p. 33): and Lemoine has shown this to be true for the decomposition of HI for pressures ranging from 0.2 to 4.5 atmospheres.

In using concentrations in place of partial pressures it is always to be remembered that the concentration (i.e., moles per liter) is the actual number of moles present divided by the total volume (see pp. 29–33). An example will perhaps make this clearer. In the reaction $A = 2B + D$, at equilibrium, we have 0.1 mole of A, 0.3 of B and .05 of D in 10 liters at atmospheric pressure and 0°. Starting with 0.5 mole of A, 0.1 of B and 0.4 of D, in 22.4 liters, find direction and extent of the reaction.

Here we must first find the constant of equilibrium for the data given at equilibrium. Since we have 0.1

nole of A in 10 liters, the concentration of A, at equilibrium is $\frac{0.1}{10}$, of B $\frac{0.3}{10}$, and of D $\frac{0.05}{10}$, hence

$$K_c = \frac{\left(\frac{0.3}{10}\right)^2 \left(\frac{0.05}{10}\right)}{\left(\frac{0.1}{10}\right)}.$$

Assuming that x moles of A are formed by the reaction, the final volume, from the 0.5 of A, the 0.1 of B, and the 0.4 of D, will be $[(0.5+x)+(0.1-2x)+(0.4-x)]$ 22.4 liters, the temperature remaining constant at 0°, i.e., $(1-2x)$ 22.4 liters. The concentrations at quilibrium, then, will be $\frac{0.5+x}{(1-2x)22.4}$ moles per liter f A, $\frac{0.1-2x}{(1-2x)22.4}$ of B, and $\frac{0.4-x}{(1-2x)22.4}$ of D, hence the lue of K_c; as found above, is to be equated to these lues in the following way:

$$K_c = \frac{\left(\frac{0.1-2x}{(1-2x)22.4}\right)^2 \left(\frac{0.4-x}{(1-2x)22.4}\right)}{\left(\frac{0.5+x}{(1-2x)22.4}\right)},$$

and the sign of x will show the direction of the reaction, and the numerical value its extent (p. 245).

Since according to the law of mass action the *concentration* is to be raised to a power, *it is the whole frac-*

m representing it which is to be so treated, i.e., the mber of moles per liter.

When applied to the equilibrium resulting from a seous dissociation the constant of the law of mass tion is usually designated as *the constant of dissocia-* *m.* From it, it is possible, just as above, to calculate e degree of dissociation from a certain amount of the ssociating substance, or how much of the products, hen present alone, or with the substance, will unite form the substance itself. And, conversely, we can lculate K_c or K_p for each of the substances for which ta was given on pages 27 and 28; and the values will dependent only upon the temperature, the units em- oyed, i.e., c or p, and nature of the substance.

Where, as is the case here, we know α, the degree of ssociation of the substance, we can proceed as follows: r the reaction

$$PCl_5 \rightleftarrows PCl_3 + Cl_2,$$

r example, we would have for concentrations the rmula

$$K = \frac{c_{PCl_3} \times c_{Cl}}{c_{PCl_5}}.$$

Starting with 1 mole of PCl_5, which, if undissociated, uld occupy V' liters at atmospheric pressure, with α

as the degree of dissociation, the concentrations, where V is the final volume, i.e. $(1+\alpha)V'$ at the same temperature and pressure, are as follows: For PCl_5, at equilibrium, $\frac{1-\alpha}{V}$, for PCl_3 $\frac{\alpha}{V}$, and for Cl_2 $\frac{\alpha}{V}$, hence K_c, which we wish to determine, is to be found from

$$K_c=\frac{\alpha^2}{(1-\alpha)V}\ \left(\text{i.e., } \frac{\alpha}{V}\times\frac{\alpha}{V}\div\frac{(1-\alpha)}{V}\right).$$

At 250° for PCl_5 $\alpha=80\%$ (page 27) and, since the pressure is atmospheric, 1 mole must be present in $22.4\frac{273+250}{273}$ liters; this is equal to V'. V, then, is equal to $(1+0.8)\left(22.4\frac{273+250}{273}\right)$, and we have as the dissociation constant for PCl_5 at 250°

$$K_c=\frac{(0.8)^2}{(1-0.8)(1+0.8)22.4\frac{273+250}{273}}.$$

From the value thus obtained we could then calculate the direction and extent of the reaction at 250° when we start with definite amounts of the three constituents, or the value of α for a different V.

A physical idea of the dissociation constant, as found for concentrations, can be obtained by aid of the formula

$K_c=\frac{\alpha^2}{(1-\alpha)V}$. Assuming that α is equal to 0.5, i.e., that the degree of dissociation is 50%, for a reaction by which 1 mole is transformed into 2, we find that $K_c=\frac{(0.5)^2}{(0.5)V}$, or $2K_c=\frac{1}{V}$. *The dissociation constant (for concentrations) of such a reaction, then, when multiplied by 2 is equal to the reciprocal of the final volume resulting from the dissociation of 1 mole into 2 to the extent of 50%.* This volume is that in which 1 mole of the original substance must be placed in order that at that temperature it may dissociate to the extent of 50% into two others. Since $\frac{1}{V}$, the reciprocal of the volume produced by the dissociation of 1 mole, is equal to C, the concentration in moles per liter, we also have $2K_c=C$. An example of the use of this relation is given by the reaction $N_2O_4=NO_2+NO_2$, for which $K_c=\frac{\alpha^2}{(1-\alpha)V}=0.0138$ (calculated from $p=182.69$ mm., $d_d=1.894$, $d_u=3.18$, i.e., $\alpha=0.69$ and $V=111$, all at 49°.7). Nitrogen tetroxide, then, should be 50% dissociated at a concentration of $2\times0.0138=\frac{1}{V}=C$ moles per liter; or at a dilution of 1 mole in 36.3 liters Experiment shows that at this temperature $\alpha=0.493$ at the dilution 1 mole in 40 liters, which, considering the single value from which K_c is determined, and the evident small error in observations, is a satisfactory agreement.

A similar physical definition could also be deduced for the reaction $A=2B+D$, where $K_c=\frac{\alpha^3}{(1-\alpha)V^2}$, but it is not so simple as the other.

It is to be noted here that the product of the substances on the right of the equation has always been placed in the numerator of the fraction giving the value of K_c or K_p (p. 241). This arrangement, of course is optional so long as it is retained the same. In the one case the value of K_c or K_p will simply be the reciprocal of that of the other.

In speaking of dissociation (p. 26) it was mentioned that the addition of one of the products of dissociation to the system, or their previous presence over the dissociating body, decreases the extent of the dissociation. That this must be true according to the law of mass action is made obvious by the consideration of any definite case.

Supposing, for example, in the case of phosphorus pentachloride, the space over it contains chlorine prior to the dissociation. Since the ratio $\frac{\text{conc. } Cl \times \text{conc. } PCl_3}{\text{conc. } PCl_5}$ must be a constant, less of the PCl_5 will dissociate, for less of it, with the chlorine already present, will suffice

A somewhat more complicated case of the application of the law of mass action to homogeneous gaseous systems is given by the dissociation of carbon dioxide, according to the scheme,

$$2CO_2=O_2+2CO.$$

If at equilibrium at any definite temperature the partial pressures are p for CO_2, p_1 for oxygen, and p_2 for CO (where these come from the CO_2), then for that temperature

$$K_p=\frac{p_1p_2^2}{p^2},$$

and if oxygen is already present, from an exterior source, to the pressure a, the decrease in the pressure of carbon monoxide due to its effect upon the dissociation can be readily calculated. We have, then, *if the volume of the system is unchanged,*

$$K_p=\frac{(p_1+a-x)(p_2-2x)^2}{(p+2x)^2},$$

from which x can be calculated (p. 245). p_2-2x will then give the partial pressure of carbon monoxide, and $p+2x$ that of carbon dioxide, in the presence of a of oxygen, the constant remaining as above.

For carbon dioxide at atmospheric pressure and 3000°, $\alpha=0.4$, i.e., 0.5 of the total pressure is due to CO_2, 0.33 to CO, and 0.17 to oxygen, consequently

$$K_p=0.074,$$

for these are partial pressures, the total pressure being 1 atmosphere.

The constant for CO_2 may also have a different value; it is that which is obtained from the formula

$$CO_2 = \tfrac{1}{2}O_2 + CO,$$

and is equal to

$$K_p = \frac{\sqrt{p_1}p_2}{p},$$

which, with the above data, leads to the value

$$K_p = 0.272.$$

Naturally, what was said above of the arrangement of the ratio expressing K also holds here. Either constant may be used for this temperature, provided that we always use the same form of relation.

This is also true for the reaction

$$N_2O_4 \rightleftarrows NO_2 + NO_2, \text{ or } N_2O_4 \rightleftarrows 2NO_2,$$

which may be written by the α formula either as

$$K_c = \frac{\alpha^2}{(1-\alpha)V} \quad \left(\text{i.e., } \frac{\alpha}{V} \times \frac{\alpha}{V} \div \frac{1-\alpha}{V}\right),$$

r

$$K_c' = \frac{4\alpha^2}{(1-\alpha)V} \quad \left(\text{i.e., } \left(\frac{2\alpha}{V}\right)^2 \div \frac{1-\alpha}{V}\right).$$

nd one form must be selected and retained.

For examples of the law as given above see Bodenstein and Pohl, Z. f. Elektrochem., 11, 373, 1905; Tower, J. Am. Chem. Soc., 27, 1209–1216, 1905; Lewis, *ibid.*, 28, 1380–1395, 1906; von Falkenstein, Z. f. Elektrochem., 12, 763–764, 1906.

59. Equilibrium in non-homogeneous systems.—As we found above (p. 117), so long as a phase of a system is present at all, its amount is without influence. For this reason the application of the law of mass action is simpler in the case of a non-homogeneous than in that of a homogeneous one, for the active mass of a solid phase remains constant so long as it is present at all, and thus can be included in the constant of equilibrium; the new value being a constant, although not the one which would be obtained were these factors regarded. As long as we have the ratio of the masses of the constituents which regulate the reaction, however, this constant value fulfils all our needs. Thus for the reaction

$$\mathrm{CaCO_3} \rightleftarrows \mathrm{CaO} + CO_2,$$

calling the constant pressures, due to gaseous $CaCO_3$ and CaO, π_1 and π_2, and that of the CO_2 p, we have, according to the law of mass action,

$$K_p = \frac{\pi_2 p}{\pi_1}.$$

but since π_1 and π_2 will remain constant at any one temperature, we may employ the simpler form

$$K_p' = p,$$

i.e., equilibrium at any one temperature depends only upon the pressure of the carbon dioxide gas produced.

In Table VI the pressures are given under which equilibrium exists at different temperatures.

TABLE VI.

EQUILIBRIUM OF $CaCO_3 \rightleftarrows CO_2 + CaO$.

Temperature ° C.	Press. mms. of Hg.	Temperature ° C.	Press. mms. of Hg.
547	27	745	289
610	46	810	678
625	56	812	753
740	255	865	1333

This means that $CaCO_3$ when heated in a vacuum to any temperature gives off CO_2, $CaCO_3$, and CaO until a certain pressure is reached. Thus at 547° a pressure of 27 mms. of Hg is produced.

See Brill, Z. f. anorg. Chem., 45, 275, 1905; and Pott, Dissertation, Freiburg, 1905.

60. Dissociation of a solid into more than one gas.—The vapor of solid NH_4HS shows by its density an almost complete dissociation into NH_3 and H_2S,

$$NH_4HS \rightleftarrows NH_3 + H_2S.$$

At 25°.1 the gaseous pressure is equal to 501 mms. of Hg, i.e., since the partial pressures of the H_2S and NH_3 are the same they are each equal to nearly 250.5 mms. of Hg. Equal only nearly, however, because this pressure includes that of the undissociated NH_4HS gas. But since this is very small and constant at any one temperature it may be neglected. If π is the partial pressure of the NH_4HS gas, and p_1 and p_2 are those of the NH_3 and H_2S, then by the law of mass action

$$K_p\pi = p_1p_2.$$

Since, however, π is constant at any one temperature, we have

$$K_p' = p_1p_2.$$

The total pressure, $P = 501$ mms., is equal, by Dalton's law, to the sum of the partial pressures, and neglecting π, we have,

$$P = p_1 + p_2$$

or

$$\frac{P}{2} = p_1 = p_2,$$

and

$$K_p' = p_1p_2 = \frac{P}{2}\frac{P}{2} = \frac{P^2}{4}$$

or

$$K_p' = \frac{P^2}{4} = \frac{(501)^2}{4} = 62750.$$

This value $K_p' = p_1 p_2$ may be verified experimentally by observing the effect of the addition to the dissociating system of one of the products of the dissociation, since the product of the partial pressures must always remain constant for constant temperature. Table VII gives the results of experiments carried out for this purpose, the pressures being mms. of Hg.

TABLE VII.

$p_1(NH_3)$	$p_2(H_2S)$	$p_1p_2 = K_p'$
208	294	61152
138	458	63204
417	146	60882
453	143	64779
		Average = 62504

The average of which agrees quite well with the value previously found. In each case a certain amount of one of the products is added before the solid is sublimed and the total pressure afterward determined. It is quite simple then to find the amount of solid which has dissociated and thus the total amount of each gas present.

Magnussen (Jour. Phys. Chem., 11, 21, 1907) has also studied this equilibrium at 20°, and finds the dissociation pressure to be 355.1 mm. This gives constant $= p_{NH_3} p_{H_2S}$, a value of 3152, which holds constant for varying amounts of NH_3 and H_2S. He experienced experimental difficulties due to the adsorption of NH_3

on the solid formed, but when allowance was made for this satisfactory agreements were observed.

The case of the dissociation of ammonium carbamate is quite similar. We have (Horstmann, Lieb. Ann., 187, 48, 1877)

$$NH_4OCONH_2 \rightleftarrows 2NH_3 + CO_2;$$

i.e.,

$$K_p\pi = p_1^2 p_2.$$

But

$$p_1^2 = \frac{P}{3}\times\frac{P}{3} = \frac{P^2}{9}, \quad p_2 = \frac{P}{3};$$

hence

$$K_p' = p_1^2 p_2 = \frac{P^3}{27},$$

(or page 255, $p_1 = \frac{2P}{3}$, and $K_p = \frac{4P^3}{27}$, but the former is the conventional form), which has been found to hold true by experiment.

The pressure produced by ammonium carbamate when heated to various temperatures is given below.

Temperature.	Gaseous Pressure.	Temperature.	Gaseous Pressure.
−15°	2.6 mm.	24°	84.8 mm.
− 5	7.5	30	124
0	12.4	40	248
2	15.7	48	402
4	19.0	50	470
10	29.8	55	600
18	53.7	60	770

Isambert has proven this relation to hold when NH_3 or CO_2 are initially present, i.e., that K_p' remains constant even after addition of one of the products of the reaction. He also proved that the presence of an indifferent gas does not affect the dissociation, for the dissociation-pressure of a substance is not changed by the presence of an indifferent gas, i.e., the partial pressures remain unaltered. Contrary to the case of a homogeneous equilibrium (pp. 252 and 253), an increase of volume has no effect upon the degree of dissociation of a non-homogeneous system, *so long as the solid (liquid) phase is present*, for the dissociation-pressure is dependent, in such systems, only upon the temperature and nature of the substance.

de Forcrand (Ann. de Chim. et de Phys. [7], 28, 545) finds for solids dissociating into gases a rule similar to Troutons (p. 69), i.e., $\frac{Q}{T}=\text{const.}=33$, where Q is the heat of dissociation of 1 mole of the solid into its gaseous products, and T is the absolute temperature at which the dissociation pressure is 1 atmosphere. But Nernst has shown that although this constant should be independent of the substance, it is dependent upon the temperature, just as Trouton's constant is. Thus $\frac{Q}{T}=29.7$ for $T=100°$; 33.6 for $T=300°$; 35.3 for $T=500°$; and 37.7 for $T=1000°$, but no general formula including the correction has as yet been derived.

61. Equilibrium in liquid systems.—The reaction

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

as already observed, reaches the state of equilibrium when we have present 1/3 mole acid + 1/3 mole alcohol + 2/3 mole ester + 2/3 mole water, provided we start with 1 mole of each of the two constituents (either acid and alcohol or ester and water).

This reaction goes very slowly at ordinary temperatures, but when it reaches the above final state it remains in it indefinitely. If we designate by v the volume of the system, and start with 1 mole of acid, m moles of alcohol, and n moles of ester (or water), then in the state of equilibrium, after x moles of alcohol have been decomposed, we shall have

$\text{alcohol} = \frac{m-x}{v}$ moles per liter.

$\text{acid} = \frac{1-x}{v}$ “ “ “

$\text{ester} = \frac{x}{v}$ or $\left(\frac{n+x}{v}\right)$ “ “ “

$\text{water} = \frac{n+x}{v}$ or $\left(\frac{x}{v}\right)$ “ “ “

hence, applying the law of mass action, we obtain

$$K_c = \frac{(n+x)x}{(1-x)(m-x)}.$$

In the special case of equilibrium above, however, $m=1, n=0, x=2/3$; hence

$$K_c = \frac{(2/3)^2}{1/3 \times 1/3} = 4.$$

This value of K_c is one of the few which are practically independent of temperature. At 10° it is found that 65.2% undergoes change, while at 220° the decomposition is but 66.5%.

This equation has been tested by experiment with very satisfactory results. *It has been found, also, as would be expected, that by using a large amount of acetic acid to a small amount of alcohol, or vice versa, the formation of ester and water is almost complete.* In the same way a large amount of water upon a small quantity of ester causes the latter to be almost entirely transformed.

In the following table some of the experimental results for this reaction are compared with the values calculated by aid of the above formula, and will serve to show how accurate this law is in its application to liquid systems.

Moles of Alcohol to 1 Mole of Acid.	Moles of Ester or Water.	
	Obs.	Calc.
0.05	0.05	0.049
0.08	0.078	0.078
0.18	0.171	0.171
0.28	0.226	0.232
0.33	0.293	0.311
0.50	0.414	0.423
0.67	0.519	0.528
1.00	0.665	0.667
1.50	0.819	0.785
2.00	0.858	0.845
2.24	0.876	0.864
8.00	0.966	0.945

Using 1 mole of acid, 1 mole of alcohol, and various amounts of water (no ester being added) we find the following results.

Moles of H_2O to 1 mole of acid + 1 mole of alcohol.	Moles of Ester Formed.	
	Obs.	Calc.
0	0.665	0.667
0.5	0.614	0.596
1.0	0.547	0.542
1.5	0.486	0.5
2.0	0.458	0.465
4.0	0.341	0.368
6.5	0.284	0.288
7.5	0.198	0.212

Amylene in contact with acid forms an ester, according to the equation

$$CH_3COOH + C_5H_{10} \rightleftarrows CH_3COO(C_5H_{11}).$$

If x is the amount of ester formed when equilibrium is established, v is the volume of the system, and 1 mole of acid is used for a moles of amylene, then

$$\frac{a-x}{v}=\text{amount of amylene left;}$$

$$\frac{1-x}{v}=\text{`` `` acid ``}$$

$$\frac{x}{v}=\text{`` `` ester formed;}$$

hence

$$K_c=\frac{xv}{(a-x)(1-x)}.$$

The value for K_c in this case has also been determined experimentally. It was found that

$$K_c=\frac{1}{.001205},$$

the constant in the form

$$K_c'=\frac{(a-x)(1-x)}{xv},$$

having the value 0.001205.

The agreement of theory and experiment in this case, the acid being trichloracetic, is shown by the following summary.

a.	v (liters).	x obs.	x calc.
2.15	361	0.762	0.762
4.12	595	0.814	0.821
4.48	638	0.820	0.826
6.63	894	0.838	0.844
6.80	915	0.839	0.845
7.13	954	0.855	0.846
7.67	1018	0.855	0.846
9.12	1190	0.857	0.853
9.51	1237	0.863	0.853
14.15	1787	0.873	0.861

As will be observed, the volume here, since there are not the same number of formula weights on both sides, must be retained in the formula.

Non-electrolytic dissociation in solution.—When a solid goes into solution its action is apparently analogous to its transformation into the gaseous state. A saturated solution, thus, in contact with the solid at any temperature will still be saturated. We have, then, by the law of mass action, for any one temperature,

$$K_c\pi = c$$

or

$$K_c' = c$$

where c is the concentration of solid in solution and varies with the temperature. If the solid in going into solution dissociates into other substances, then an addition of one of these will cause less substance to dissolve.

This has been proven by Behrend for a solution of phenanthrene picrate in absolute alcohol, in which a decomposition into phenanthrene and picric acid takes place to a large extent.

By the law of mass action

$$K_c c = c_1 c_2,$$

where c = undissociated phenanthrene picrate, c_1 = free picric acid, and c_2 = free phenanthrene—all expressed in moles per liter. For any one temperature c must be constant, since the solution is saturated; hence

$$c_1 c_2 = \text{constant}.$$

Coefficient of partition or distribution. We have already considered the distribution of a substance between two non-miscible solvents in the case that the formula weight is the same in each (pp. 201–202); now we must find the effect of a difference in the formula weight. Let the heterogeneous reaction be

$$A_n \rightleftarrows nA,$$

i.e., let the molecular weight in the one layer be A_n, and in the other, non-miscible. one A. By the law of mass action, we have, then,

$$K_c = \frac{c_A{}^n}{c_{A_n}},$$

or, since $c_A=\frac{w_A}{M_A}$, and $c_{A_n}=\frac{w_{A_n}}{M_{A_n}}$,

$$K_c=\left(\frac{w_A}{M_A}\right)^n \Big/ \frac{w_{A_n}}{M_{A_n}},$$

and

$$\frac{M_A{}^n}{M_{A_n}}\cdot K_c=\frac{w_A{}^n}{w_{A_n}}.$$

When the formula weight in the one solvent is always n times that in the other (at the dilutions considered), the ratio of distribution in the form $\frac{w_A{}^n}{w_{A_n}}$ *will remain constant, independent of the original dilution.*

If the simple ratio $\frac{w_A}{w_{A_n}}$ is constant at all dilutions, then, the molecular weights in the two solvents must be identical, i.e., n must equal 1 in the above chemical reaction. In connection with possible errors in this method see Bancroft, J. phys. Chem., 12, 30–35, 1908.

If the formula weight in one is twice that in the other, then it is obvious that $k'c_2=c_1{}^2$, i.e., that $\frac{c_1{}^2}{c_2}$ and $\frac{c_1}{\sqrt{c_2}}$ are constant, for all dilutions. An illustration of this is given by the distribution of benzoic acid between water (c_1) and benzene (c_2), the values of $\frac{c_1}{c_2}$ being 0.062, 0.048, and 0.030, while those of $\frac{c_1}{\sqrt{c}}$, for the same dilutions, are

0.0305, 0.0304, and 0.0293. Benzoic acid, then, has twice the molecular weight in benzene that it has in water, a fact which has been proven by the freezing-point method.

(For illustrations of the above law see Nernst, Zeit. f. phys. Chem., 8, 110, 1891; Aulich, *ibid.*, 8, 105, 1891; Hautzsh and Sebalt, *ibid*, 30, 268, 1896; Hantzsh and Vagt, *ibid.*, 38, 705, 1901; Herz and Fischer, Ber. 38, 1138, 1905; Herz and Lewy, Zeit. f. Elektrochem., 11, 818, 1905; Dawson, Trans. Chem. Soc., 89/90, 1666–1674, 1906; Morgan and Benson, Jour. Am. Chem. Soc., 29, 1176–1179, 1907; and others.)

This law is very useful for the determination of a constituent in a solution which cannot be found readily in any other way. Thus aniline hydrochloride in water reacts to form hydrochloric acid and free aniline, and the concentration of aniline can be found by distribution between water and benzene (see hydrolytic dissociation).

62. The effect of temperature upon an equilibrium. The variation of the constant of equilibrium or dissociation with the temperature.—In the case of an invariant equilibrium under constant pressure a change in the temperature causes one of the phases to disappear entirely. In the case of a univariant equilibrium, however, the effect is quite different. A very small change in temperature causes only a very slight change in the equilibrium. This causes a corresponding change in the relative composition of the reacting constituents, in one direction or the other, which just compensates the change which the reaction coefficient has suffered.

By differentiating equation (18) (p. 241) by the aid of (19) we obtain

$$dW = RdT \log_e K_p + RTd(\log_e K_p).$$

But by the second principle (p. 58)

$$dW = Q\frac{dT}{T},$$

where dW is the former dQ, i.e., the work in terms of heat.

Combining these two equations, we get

$$Q = RT \log_e K_p + \frac{RT^2 d(\log_e K_p)}{dT}.$$

Since W expresses the work which is done by the transfer of the total heat Q, the difference, $Q - W$, is equal to the portion of the heat absorbed which is not transformed into work. Since in thermo chemical calculations we reckon heat absorbed as negative, this value, $Q - W$, is *the negative heat of the reaction, under constant pressure conditions.* We have thus by (18)

$$-Q = W + \frac{RT^2 d(\log_e K_p)}{dT},$$

$$-(Q - W) = -q_p = RT^2 \frac{d}{dT}(\log_e K_p),$$

or (21) $$\frac{d}{dT}(\log_e K_p) = -\frac{q_p}{RT^2},$$

ince $K_c=(RT)^{\Sigma n-\Sigma n'}K_p$ (p. 242), i.e., to K_p multi- d by RT raised to a power equal to the difference veen the total initial and total final moles, as shown he chemical equation, we have, substituting K_c for K_p

$$\frac{d}{dT}(\log_e K_c-\log_e(RT)^{\Sigma n-\Sigma n'}) = -\frac{q_p}{RT^2},$$

$$\frac{d}{dT}\log_e K_c-\frac{(\Sigma n-\Sigma n')dT}{T} = -\frac{q_p}{RT^2},$$

$$\frac{d}{T}\log_e K_c=-\frac{q_p}{RT^2}+\frac{\Sigma n-\Sigma n'}{T}=\frac{(\Sigma n-\Sigma n')RT-q_p}{RT^2}.$$

e the term $(\Sigma n-\Sigma n')RT$, by definition, is simply expression of the external work done upon or by the em, hence, since it is equal to $-nRT$ (page 224), have

$$-nRT-q_p=-q_v;$$

we may write

$$\frac{d}{dT}\log_e K_c=-\frac{q_v}{RT^2}.$$

o integrate these expressions it is necessary to assume q itself is independent of the temperature. This undoubtedly be practically true for small temperature rvals; for larger ones, however, we must be satisfied btain q as the value for the temperature which is the n of the two extreme temperatures.

By integration of (21) and (22) on the above assumption, we find

$$\log_e K_{p'} - \log_e K_p = \frac{q_p}{R}\left(\frac{1}{T'} - \frac{1}{T}\right),$$

and

$$\log_e K_{c'} - \log_e K_c = \frac{q_v}{R}\left(\frac{1}{T'} - \frac{1}{T}\right).$$

Or, using ordinary logarithms, and solving for q, we obtain

$$(23) \qquad q_p = \frac{R \times 2.306(\log K_{p'} - \log K_p)TT'}{T - T'} \text{ cals.,*}$$

and

$$(24) \qquad q_v = \frac{R \times 2.306(\log K_{c'} - \log K_c)TT'}{T - T'} \text{ cals.,*}$$

where $R = 2$ cals.

The heat evolved by a reaction at $\frac{T+T'}{2}$, *under constant pressure (external work) conditions, i.e.,* q_p, *can be calculated from the equilibrium constants for pressures* ($K_{p'}$ *and* K_p) *at the two temperatures* T' *and* T; *or, knowing* q_p *and* K_p *at one temperature we can calculate* $K_{p'}$ *at the other.*

The heat of reaction at $\frac{T+T'}{2}$ *and constant volume (no external work) conditions, i.e.,* q_v, *can be calculated in a*

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* For another form of this equation see Nernst's "Experimental Applications of Thermodynamics in Chemistry." Scribner, 1907.

milar manner from the equilibrium constants for con-ntrations, $K_{c'}$ and K_c at T' and T.

The value of q in these relations is for the reaction of ıich the K values are expressive. Thus in the reaction

$$2A=B+C,$$

heat q would be for 2 moles of A if $K=\frac{B\times C}{A^2}$ were d, and for 1 mole of A if the K values used were tten $K=\frac{\sqrt{B}\sqrt{C}}{A}$.

ne consequence of these formulæ is of special impor-ce. If q is zero, the value of K does not change as result of a change in temperature. Thus the re-on between acid and alcohol, mentioned above 263), the mutual transformation of optical isomers, a number of others, are found neither to absorb nor erate heat, nor to suffer a displacement of equilibrium, a change in the value of K, by a change in tempera-e.

Ve shall now consider the method of applying these mulæ for various purposes to various equilibria.

Vaporization.—The condition regulating the equi-rium between a liquid and its vapor (a univariant stem) is the pressure of the latter, and this depends pon the temperature. We have then

$$K_p=p, \text{ and } K_{p'}=p'.$$

Regnault found for water,

$$T=273, \quad p=4.54 \text{ mms. of Hg.}$$

$$T'=273+11.54, \quad p'=10.02 \text{ mms. of Hg.}$$

We have then

$$q_p=\frac{2\times 2.306(\log 10.02-\log 4.54)273\times 284.5}{273-284.5}$$
$$=-10670 \text{ cals.}$$

where direct experiment at constant pressure gives -10854 cals.

Dissociation of solids.—If a solid dissociates into gases, the equilibrium is conditioned by the concentration of the latter. If in the dissociation

$$\mathbf{NH_4HS} \rightleftarrows H_2S+NH_3$$

c_1 and c_2 are the concentrations of H_2S and NH_3, that of the NH_4HS being small and remaining constant, then (p. 260)

$$\pi K_p'=\left(\frac{p}{2}\right)^2 \quad \text{and} \quad \pi' K'_{p'}=\left(\frac{p'}{2}\right)^2,$$

and $\pi K'_p$ and $\pi' K'_{p'}$ can be used for K_p' and $K'_{p'}$ in the ratio if π does not vary greatly with the temperature. From

$$T=273+\ 9.5, \quad P\ =175 \text{ mms. of Hg;}$$
$$T'=273+25.1, \quad P'=501 \text{ mms. of Hg;}$$

e have then

$$q_p=\frac{2\times2.306\left(\log\left(\frac{501}{2}\right)^2-\log\left(\frac{175}{2}\right)^2\right)282.5\times298.1}{282.5-298.1}$$
$$=-22740 \text{ cals.},$$

hile direct experiment, under constant pressure leads -22800 cals. per mole.

Solution of solids.—In this case the equilibrium depends ly upon the concentration of solid substance in the lution, and the temperature; we have, then,

$$K_c=c, \quad K_{c'}=c',$$

here c and c' are the concentrations of a saturated solu- n at the temperatures T and T'.

van't Hoff found by experiment with succinic acid water that

for $T=273$, $c=2.88$ moles per liter;

d for $T'=273+8.5$, $c'=4.22$ moles per liter.

For 1 mole, then, by (44),

$$q=-6900 \text{ cals.},$$

ile Berthelot found -6700 cals. by direct experiment. is of course is also the value for constant volume, r the external work by the change in volume is utterly gligible.

Ionization of solids in solution.—If a substance is very slightly soluble, then the solution must contain principally ions and very little undissociated substance, and the heat of dissociation must be the same as the heat of solution, i.e., equal to the negative value of the heat of precipitation from the free ions. Thus for AgCl we have

$$AgCl = Ag^{\cdot} + Cl'.$$

If the solubility at $T = c$, and at $T' = c'$, in moles per liter, then, since 2 moles of the ions form from 1 mole of the salt, we have

$$K_c = c_{ag} \times c_{cl} = c^2_{salt},$$

and

$$K_{c'} = c'_{ag} \times c'_{cl} = c'^2_{salt}.$$

For
$$T = 273 + 20, \quad c = 1.10 \times 10^{-5},$$
$$T' = 273 + 30, \quad c' = 1.73 \times 10^{-5};$$

hence $q_v = -15900 = -159K$.

For the negative heat of precipitation we found (p. 233) $-158K$, which is an excellent agreement.

Dissociation of gaseous bodies.—Under constant atmospheric pressure the gas N_2O_4 dissociates into NO_2, according to the scheme

$$N_2O_4 \rightleftarrows 2NO_2.$$

The following results are observed:

$$T=273+26.1, \quad \alpha=0.1986,$$

$$T'=273+111.3, \quad \alpha=0.9267.$$

Since here the total pressure is 1 atmosphere, the partial pressures are

$$p_{N_2O_4}=\frac{1-\alpha}{1-\alpha+2\alpha}\times 1 \text{ atmos.}$$

and

$$p_{NO_2}=\frac{2\alpha}{1-\alpha+2\alpha}\times 1 \text{ atmos.}$$

For K_p and K_p' we then have the values

$$K_p=\left(\frac{2\alpha}{1+\alpha}\right)^2\bigg/\frac{1-\alpha}{1+\alpha}=\frac{4\alpha^2}{1-\alpha^2},$$

and

$$K_p'=\left(\frac{2\alpha'}{1+\alpha'}\right)^2\bigg/\frac{1-\alpha'}{1+\alpha'}=\frac{4\alpha'^2}{1-\alpha'^2},$$

hence

$$q_p=\frac{2\times 2.306\left(\log\frac{4\times 0.9267^2}{1-0.9267^2}-\log\frac{4\times 0.1986^2}{1-0.1986^2}\right)299.1\times 384.3}{299.1-384.3}$$

$$=-12260 \text{ cals. per mole of } N_2O_4.$$

No direct determination of this heat of dissociation has been made.

For other examples of such calculations see Bodenstein and Pohl (Zeit. f. Elektrochem., 11, 373, 1905, and Lewis (Jour. Am. Chem. Soc., 28, 1380, 1906).

B. CHEMICAL KINETICS

63. Application of the law of mass action.—Thus far we have only considered the equilibrium which is attained *after* the reaction has come to rest, i.e., after the two sides bear a constant relation to one another. The question now arises as to the progress of a reaction toward this state, and the factors upon which the time necessary to attain it depends.

By aid of the law of mass action, it is possible to find an answer to both portions of this question. Since chemical action at any time, according to it (p. 238), is proportional, for constant temperature, to the active masses of the substances present, i.e., to those portions which are free to act, then, when we have two substances reacting, the concentrations being a_1 and a_2 moles per liter,

$$\frac{dx}{dt} = k(a_1 - x)(a_2 - x),$$

where x is the fraction of a mole of each which decomposes in the time t. The term k in this equation is known as the ***speed constant*** of the reaction, and is constant at any one temperature for any value of x in the reaction in question.

Suppose we have the reversible reaction

$$A_1+A_2 \rightleftarrows A_1'+A_2',$$

which after a time attains a state of equilibrium in which all four products are present. The relative amounts of these are dependent upon the value of K_c for this reaction at this temperature according to the relation

$$K_c=\frac{c_1'c_2'}{c_1c_2}.$$

If we start with a_1 moles of A_1 and a_2 moles of A_2, then

$$\frac{dx}{dt}=k(a_1-x)(a_2-x).$$

But if we start with a_1' moles of A_1' and a_2' of A_2', then

$$\frac{dx'}{dt}=k'(a_1'-x')(a_2'-x'),$$

where $\frac{dx'}{dt}$ is the velocity in the opposite direction.

Starting with the substances on either side, then, those on the other will exert an ever-increasing influence upon the velocity due to the initial substances, and this velocity must decrease continually. Finally, however, equilibrium will be attained and the ratio of the amounts on the two sides will remain constant, i.e., the reaction as a whole ceases, and any motion which exists is so compensated by a contrary one that it does not appear.

Imagine we start with a_1 moles of A_1 and a_2 moles of A_2. The total velocity due to these at any one time will be

$$\frac{dX}{dt}=\frac{dx}{dt}-\frac{dx'}{dt}=k(a_1-x)(a_2-x)-k'(x)(x),$$

and at equilibrium, i.e., where $\frac{dX}{dt}=0$,

$$k(a_1-x)(a_2-x)=k'x^2,$$

or

$$\frac{k}{k'}=K_c=\frac{x^2}{(a_1-x)(a_2-x)},$$

i.e., *the equilibrium constant, K_c, of any reversible reaction is equal to the ratio of the speed constants of that reaction for the two directions.*

This has been proven to be true for a number of cases. For the system acid-alcohol (p. 262) it was found for a certain strength acid that $k=0.000238$ and $k'=0.000815$, from which $K_c=\frac{k}{k'}=2.92$, while direct experiment gave $K_c=2.84$.

All this is only true, however, when the reaction takes place isothermally, i.e., when the heat liberated or absorbed is removed or supplied and no change in the temperature results, for the constants k and k' are dependent upon the temperature.

In general the application of this formula is very much simplified by the fact that most reactions are almost complete in one direction, so that the second term will be so small that it may be neglected. We have then

$$\frac{dx}{dt}=k(a_1-x)(a_2-x).$$

In all these cases the values on the right are obtained by subtracting the loss from the concentration of the original substance and having as many such terms as there are moles in the formula. Thus for the reaction $A=2B+D$ we would write

$$\frac{dx}{dt}=k(c_B-x)(c_B-x)(c_D-x).$$

This is simply custom (see p. 255), for we could also write it

$$\frac{dx'}{dt}=k'(c_B-2x)^2(c_D-x),$$

and although the k value would be different, it would be constant.

64. Reactions of the first order.—For convenience we shall divide all reactions into orders. Thus a reaction of the first order is one in which but one substance suffers a change in concentration. This definition is to be further restricted, in that for the first order it is necessary that the equation show but 1 mole of one substance changing its concentration.

Cane-sugar in water solution is transformed in the presence of acids almost completely into dextrose and lævulose; it is inverted. The speed of the reaction is very small and increases with the amount of acid added.

The progress of the reaction may be observed by aid of the polariscope. The uninverted portion revolves the plane of polarization to the right, while the two products revolve it to the left. If α_0 is the positive angle of revolution at the time $t=0$, i.e., that which is due to the uninverted sugar alone, the amount of which is a moles, a_0' is the negative angle after complete inversion, and α is the angle at the time t, then since the revolution is proportional to the concentrations, x, the amount inverted, is found from

$$x=a\frac{\alpha_0-\alpha}{\alpha_0+\alpha_0'}.$$

For the time $t=0^\circ$, $\alpha=\alpha_0$, i.e., $x=0$; for the time $t=\infty$, i.e., after complete inversion, $\alpha=-a_0'$ or $x=a$.

This process was first measured by Wilhelmy (1850), nd it has played an important rôle in the history of hemical mechanics.

The process follows the scheme

$$C_{12}H_{22}O_{11}+H_2O=2C_6H_{12}O_6$$

whether acid is used or not, for the concentration of the latter does not change during the reaction. According to the law of mass action the speed is proportional to the amounts of sugar and water. The latter, however, is present in such an excess that its action may be regarded as constant. The speed of reaction, then, is proportional to the amount of sugar present and we have a reaction of the first order, i.e., the formula is

$$\frac{dx}{dt}=k(a-x),$$

where, for $t=0$, $x=0$, and k is the ***inversion constant,*** which depends only upon the temperature. By integration this becomes

$$-\log_e(a-x)=kt+\text{constant},$$

or since, for $t=0$, $x=0$,

$$\log_e(a)=\text{the constant},$$

i.e.

$$k=\frac{1}{t}\log\frac{a}{a-x}=\frac{1}{t}\log_e\frac{\alpha_0+\alpha_0'}{\alpha+\alpha_0'};$$

in other words, a constant fraction of the total amount of sugar is inverted in each unit of time.

The meaning of the constant k in words is as follows: *Its reciprocal value multiplied by the natural logarithm of 2 gives the time in minutes which is necessary for the transformation of one half the total amount of substance, provided the products of the reaction are removed as soon as they are formed and the substances replaced as they are used.* This is shown by the substitution of $\frac{a}{2}$ for x. Further, for all reactions of the first order, *this constant k is independent of the original concentration of the substance.* Table VIII gives the values for k for a 20% sugar solution in presence of a 0.5 N. solution of lactic acid at 25° C

TABLE VIII.

INVERSION OF SUGAR.

t (minutes).	a.	$\frac{1}{t}\log_{10}\frac{a}{a-x}$.
0	34°.5	......
1435	31°.1	0.2348
4315	25°.0	0.2359
7070	20°.16	0.2343
11360	13°.98	0.2310
14170	10°.01	0.2301
16935	7°.57	0.2316
19815	5°.08	0.2291
29925	− 1°.65	0.2330
∞	−10°.77	......

Since only the constancy of the term $\frac{1}{t}\log_e\frac{a}{a-x}$ is to be shown, the more convenient system of logarithms, i.e., that of Briggs, has been employed above.

65. Catalytic action of hydrogen ion. Catalysis.—The inversion of sugar, as well as all other reactions of the first order which are hastened by the action of acids, is apparently due to the ionized hydrogen which is present. This action is known as a catalytic action of the acid present, which retains throughout the reaction its original concentration. The reason why $H^{\cdot}$ ion should act in this way is unknown; but that it does have an accelerating effect is an established fact.

In general a catalytic action is one that hastens the reaction in which it is without at the same time having its concentration changed by the reaction. An example of such an action is given by the increased speed of solution of metallic mercury, silver, or copper in a nitric-acid solution in which one of these has already been dissolved to a slight extent. The catalytic action here is due to the formation of the oxides of nitrogen, these, when passed into the nitric acid from an exterior source, causing the same action as the above.

Since the catalysor takes no part in the reaction it does not alter the equilibrium constant, hence it must also hasten the reverse action, so that $\frac{k}{k'}$ may remain constant.

As there is no general law known for catalytic action the reader must be referred elsewhere for the vast number of isolated facts.

The more concentrated the acid used the more rapidly the sugar is inverted, without, however, any exact proportionality. The inverting action increases more rapidly than the concentration. In presence of a neutral salt of the acid its inverting power is increased by about 10% for the stronger acids, but decreased for the weaker ones.

Since the acceleration of the speed of the reaction is caused only by acids, and since they are distinguished by the presence of $H^{\cdot}$ ion, the peculiar action must be due to it. Further than this, a series of acids arranged in the order of inverting power is found to be in the same order in which they stand in reference to ionization. Thus it is plain that $H^{\cdot}$ ion has this effect, although in concentrated solutions the inverting power is not strictly proportional to the ionization. For example, a 0.5 N. solution of HCl inverts 6.07 times as rapidly as one of a 0.1 N. solution, while it contains only 4.64 times as much ionic $H^{\cdot}$. Arrhenius found the presence of other ions to increase the catalytic action of that of $H^{\cdot}$.

That the speed of reaction increases more rapidly than the concentration of $H^{\cdot}$ ion is assumed to be due to the fact that the negative ions are also present to an equal amount and so increase the inverting action of $H^{\cdot}$ ion.

In the presence of a neutral salt, then, we have two separate actions upon the acid: the first causes a decrease in the concentration of H˙ ion of the acid (see p. 186); the second accelerates the action of the H˙ ion left.

The stronger acids are less influenced by the former than the weaker ones, because they are dissociated more nearly to the extent to which their salts are. Consequently the second action predominates, and we have the greatest inverting power for the strong acids when a salt is present.

For the weaker acids, however, the second action is the smaller; hence the inverting action is less for weak acids in presence of a salt.

Palmaer has found that in dilute solutions, when the influence of the neutral-salt action is avoided, the inversion constant is exactly proportional to the concentration of hydrogen ions.

Another reaction of the first order which depends for its speed upon the catalytic action of H˙ ion is the formation of alcohol and acid from an ester. For example,

$$CH_3COOC_2H_5 + H_2O = CH_3COOH + C_2H_5OH.$$

The equation is the same as before, i.e., follows the law

$$k = \frac{1}{t} \log_e \frac{a}{a-x},$$

where a is the amount of ester in moles at the time $t=0$, and x is the amount transformed at the time t, and is equal also to the amount of acid or alcohol formed by the reaction during the time *t*. The progress of this reaction is observed by titrating the amount of free acetic acid present.

Ostwald measured the value for the reaction with methylacetate. He started with 1 c.c. of methylacetate and 10 c.c. HCl (1 mole to the liter), diluted to 15 c.c. To neutralize this acid 13.33 c.c. of a $Ba(OH)_2$ solution would be necessary. The amounts of acetic acid formed are shown by titration after substracting 13.33; these amounts, expressed in c.c. of $Ba(OH)_2$ solution, for various times are as follows:

0	14	34	199	539	∞	Minutes
—	0.92	2.14	8.82	13.09	14.11	c.c.

The amount of ester (a) is represented, then, by 14.11 $a-x$ being this value minus 0.92, 2.14, etc. The values thus determined for k are 0.00209, 0.00210, 0.00214, and 0.00212.

Another reaction which gives a constant when considered as a reaction of the first order is the one which is usually written

$$4AsH_3 = As_4 + 6H_2.$$

Since at 310° this fulfils the definition of a reaction of the first order, it should be written not as above, as of the fourth order, but as of the first, i.e.

$$AsH_3 = As + 1\tfrac{1}{2}(H_2).$$

Here also the velocity is exactly proportional when the action of the neutral salt is avoided. If the amount of neutral salt in the solution is so large that it can be considered constant, then a constant value will be obtained for *k*, although its absolute value will be different from that for the case that no neutral salt is present. Walker used this method to determine the concentration of H˙ ion present in a solution due to hydrolytic dissociation, which we shall discuss in detail below; and Bredig and Fraenkel (Z. f. Elektrochem., 11, 525–529, 1905) advocate for this purpose diazoacetic ester as a very accurate means of estimating concentrations of H˙ ion of *n*/1000 and less.

66. Reactions of the second order.—Here two moles of substance suffer a change in concentration during the reaction, i.e., the constant depends upon the concentration of two substances. We have then

$$\frac{dx}{dt}=k(a-x)(b-x),$$

or

$$-\frac{1}{a-b}[\log_e(b-x)-\log_e(a-x)]=kt+\text{constant}.$$

For $t=0$, $x=0$, and the constant is

$$-\frac{1}{a-b}(\log_e b-\log_e a);$$

i.e.,

$$k=\frac{1}{\quad}\log_e\frac{(a-x)b}{\quad}$$

If we use equivalent amounts of the two substances, then $a=b$, and we have

$$\frac{dx}{dt}=k(a-x)^2,$$

or

$$k=\frac{1}{t}\frac{x}{(a-x)a}.$$

Here k is inversely proportional to the original concentration.

An example of a reaction of the second order is

$$CH_3COOC_2H_5+NaOH=CH_3COONa+C_2H_5OH.$$

Table IX gives the value of this constant as calculated for different lengths of time at the temperature of 10° C.

TABLE IX.

t (minutes).	Amount NaOH in c.c. of acid.	k.
0	61.95	....
489	50.59	2.36
1037	42.40	2.38
2818	29.35	2.33
∞	14.92	....

The question as to how the speed varies with the nature of the base used has been investigated quite thoroughly. Thus Reicher (Lieb. Ann., 128, 257, 1885) and Ostwald (J. pr. Chem., 35, 112, 1887) found for strong bases (those which are much dissociated) approximately equal values for *k*; for weak ones, however, he found very much smaller values. Ostwald observed that the weak bases ammonia and allylamine fail to give a constant value for *k*. Thus for ethyl acetate and ammonia he found the values given in Table X.

TABLE X.

t (minutes).	*k*.
0	.....
60	1.64
240	1.04
1470	0.484

This failure to give a constant he recognized, however, as being due to the effect of the neutral salt formed (ammonium acetate) upon the weak base. When a large amount of this is present a constant is obtained, as is shown by Table XI.

TABLE XI.

t (minutes).	*k*.
0	.....
994	0.138
6874	0.120
15404	0.119

This shows still a slight effect of the neutral salt formed, for it is impossible to keep it perfectly constant.

Arrhenius found that the base acts simply in proportion to the amount of ionized OH′ it contains, i. e., we have

$$C_2H_3O_2C_2H_5 + OH' + Na^{\cdot} = C_2H_3O_2' + Na^{\cdot} + C_2H_5OH.$$

According to this, all bases containing the same amount of OH′ ion should give the same constant. We can rearrange our equation, then, to the form

$$\frac{dx}{dt}=k'\alpha(a-x)(b-x),$$

where α is the degree of dissociation of the base. Since the strong bases are but slightly influenced by the addition of salts with an ion in common, the constant of KOH can be taken, with very little error, to be that due to a certain concentration of OH′ ion. From this it is then possible to calculate the constant for NH_4OH, with or without an ammonium salt present. A *m*/40 solution of KOH at 24°.7 C. gives a constant equal to 6.41. Such a solution of NH_4OH is but 2.69% dissociated, while that of KOH is 97.2% dissociated. The constant, then, for NH_4OH in the absence of salt is

$$k_{NH_4OH} : k_{KOH} : : 0.0269 : 0.972,$$

or

$$k_{NH_4OH}=\frac{0.0269}{0.972}6.41=0.177.$$

The effect of the neutral salt upon the NH_4OH can be readily calculated from the dissociation of the two; we have, then, the constant for NH_4OH in presence of a neutral salt,

$$k'_{NH_4OH}=\frac{\alpha}{0.972}6.41,$$

here α is the concentration of OH′ ion in the H_4OH in presence of the amount of the neutral salts, ie concentration of which is designated below by s. able XII compares the values thus obtained with those ctually observed by experiment.

TABLE XII.

SPEED OF REACTION CAUSED BY NH_4OH.

s	a	k (calculated)	k (observed)
0	2.69%	0.177	0.156
0.00125	1.21	0.08	0.062
0.005	0.71	0.047	0.039
0.0175	0.118	0.0078	0.0081
0.025	0.082	0.0054	0.0062
0.05	0.042	0.0028	0.0033

This is a very good agreement, considering the possible experimental errors, so that we may conclude that *the velocity of saponification is proportional to the concentration of OH′ ion present, and independent of the radical by which it is accompanied.*

In a second order reaction the effect of either constituent upon the velocity should be the same.

67. Reactions of the third order.—If the 3 substances are present in equimolecular amounts, we have

$$\frac{dx}{dt}=k(a-x)^3,$$

or

$$k=\frac{1}{t}\frac{x(2a-x)}{2a^2(a-x)^2}.$$

One reaction of this order has been studied by Noyes (Zeit. f. phys. Chem , 16, 546, 1895). The reaction is

$$2FeCl_3+SnCl_2=2FeCl_2+SnCl_4,$$

or

$$2Fe^{\cdot\cdot\cdot}+Sn^{\cdot\cdot}=2Fe^{\cdot\cdot}+Sn^{\cdot\cdot\cdot\cdot}$$

The results, starting with a concentration of .025 moles of each, $SnCl_2$, $FeCl_3$, $SnCl_4$ and $FeCl_2$, were as follows:

Time	x	$a-x$	k
2.5	0.00351	0.02149	113
3	0.00388	0.02112	107
6	0.00663	0.01837	114
11	0.00946	0.01554	116
15	0.01106	0.01394	118
18	0.01187	0.01313	117
30	0.01440	0.01060	122
60	0.01716	0.00784	122
		Average =	116

For such a reaction of the 3d order k is inversely proportional to the square of the original concentration; and k for a reaction of the nth order would be inversely proportional to the $(n-1)$ power of the original concentration.

In a third order reaction the effect of the addition of one constituent on the velocity should not be the same as that produced by an excess of the other; for the above, indeed, Noyes found that an excess of ferric chloride has a greater effect in hastening the reaction than one of stannous chloride has.

Reactions of the fourth, fifth, and higher orders have also been investigated. Examples of the fourth order are as follows: The decomposition of $KClO_3$ at 395° which takes place according to the scheme

$$4KClO_3 = KCl + 3KClO_4$$

(Scobai, Zeit. f. phys. Chem., 44, 319, 1903); the reaction between hydrobromic and bromic acids, under certain conditions (Walker and Judson, Trans. Chem. Soc., 73, 410, 1898); the action of chromic acid upon phosphoric acid (Viard, C. r., 124, 148, 1897); and the reaction between bromine and benzene (Bruner, Zeit. f. phys. Chem., 41, 513, 1902).

An example of a reaction of the fifth order, which has been studied by Donnan and Le Rossignol (Trans. Chem. Soc., 83, 703, 1903) is the action of potassium ferricyanide upon potassium iodide. And one of the eighth order, which has very recently been studied by Luther and MacDougal (Zeit. f. phys. Chem., 62, 199–243, 1908) is the action of chloric acid upon hydrochloric acid, and may be written in its ionic form as follows:

$$4H^{\cdot} + 2ClO_3{}' + 2Cl' \rightarrow 2ClO_2 + Cl_2 + 2H_2O.$$

For a different handling of the fundamental differential equations of chemical kinetics, than the above, see Bray (Jour. Phys. Chem., 9, 573–587, 1905) and De Lury (*Ibid.*, 10, 423–444, 1906).

68. Incomplete reactions.—Thus far we have considered the speed of reactions which are complete, i.e., those which only cease when all the original substance has been transformed. In the case where this is not true it is necessary to use the equation in its original form. Such a case is the one already studied,

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

which goes with a certain speed until two thirds of the acid and alcohol are decomposed. When the amount of ester is equal to x, then (p. 262)

$$\frac{dx}{dt} = k(1-x)^2 - k'x^2.$$

When we start with 1 mole of each acid and alcohol and have no water or ester present, and k and k' are the speed components in the two directions, we have as above (pp. 280–281)

$$K = \frac{k}{k'} = 4.$$

erving the change for any time we find

$$k-k'=\frac{3}{4t}\log_e\frac{2-x}{2-3x}.$$

hese two values $\frac{k}{k'}$ and $k-k'$ we can find k. The n so measured, however, does not give a con- alue for k. This was accounted for by Kistia- (Wied. Beibl., 1891, p. 295) and Knoblauch (Z. f. hem., 22, 268, 1897). When alcohol and acetic rm ester and water the reaction goes faster than ld, according to the theory. This is due to the ic action of the H· ion present when the reaction the one direction. If, then, the concentration ion is retained the same throughout the reaction, ld be constant, which has been found by experi- be the case.

shows the importance of secondary reactions, may give entirely false results unless accounted

Heterogeneous systems.—The solution of a sub- in an acid depends for its speed upon the surface act between the two and upon the strength of the but many secondary reactions can take place here, our results are only approximate.

e assume the surface to be so large that it changes but slightly during the reaction we may consider it as constant; we have then, if S is the surface,

$$\frac{dx}{dt}=kS(a-x),$$

where x is the amount dissolved in the time t. By integration we find

$$kS=\frac{1}{t}\log_e\frac{a}{a-x}.$$

The formula in this form was found by Boguski (Ber., 9, 1646, 1876; *ibid.*, 10, 34, 1877) to give constant results, within the experimental error, for the solution of marble in acid. Noyes and Whitney (Zeit. f. phys. Chem., 23, 689, 1897) have proved that the speed of solubility of a solid substance in any instant is proportional to the difference between the concentration of saturation and the one at the time of the experiment. Further work of this sort has been done by Bodenstein and others, see Zeit. f. phys. Chem., 60, 1–67, 1907; 53, 166, 1905; 49, 41, 1904; and 46, 725, 1903.

70. **Speed of reaction and temperature.**—Empirically it has been found that *the speed of a reaction always increases with an increase in the temperature.* The increase in many cases is very great. Thus a rise in temperature of 30° causes the speed of sugar inversion to be five times as great as before. An empirical formula was found by van't Hoff and tested by Arrhenius. We have

$$C_1=C_0e^{A(T_1-T_0)/T_0T_1},$$

where C_0 is the speed constant at the temperature T_0,

C_1 is the constant at T_1, e is the base of the natural logarithms, and A is a numerical constant. Using the lower of two temperatures as T_0, we have for the transformation of ammonium cyanate into urea

$$T_0 = 273 + 25^\circ, \quad C_0 = 0.000227, \quad A = 11700.$$

T_1	C (obs.)	C (calc.)
273+39	0.00141	0.00133
273+50.1	0.00520	0.00480
273+64.5	0.0228	0.0227
273+74.7	0.062	0.0623
273+80	0.100	0.105

C. APPLICATION OF THE LAW OF MASS ACTION TO ELECTROLYTES—IONIC EQUILIBRIA.

71. Organic acids and bases. The Ostwald dilution law.—The application of the law of mass action to gaseous equilibria, as well as to those existing in solutions of non-electrolytes—in short to chemical equilibria—has shown that it is a general law of nature, holding between very wide limits. The question which naturally arises here, then, is, Can the law of mass action also be applied to those equilibria existing between the ionized and un-ionized portions of a substance in solution? In other words, is the law of mass action the principle governing the amounts of these portions which can exist together in equilibrium? It is the purpose of this section to answer this question so far as is possible from our pre knowledge of the facts.

The conductivity ratios $\frac{\mu_v}{\mu_\infty}$, as well as the methods determining the average molecular weight, where th can be carried out with sufficient accuracy, show that water solution of acetic acid is ionized according to t following scheme:

$$CH_3COOH \rightleftarrows CH_3COO' + H^{\cdot}.$$

From this equation, applying the law of mass-action, we obtain

$$K_c = \frac{c_{CH_3COO'}c_{H^{\cdot}}}{c_{CH_3COOH}} = \text{constant},$$

or (see page 249)

$$K_c = \frac{\alpha^2}{(1-\alpha)V} = \text{constant},$$

which is known as the *Ostwald dilution law*, for it gives the relation of ionization to dilution.

Substituting the ratio $\frac{\mu_v}{\mu_\infty}$ for α at various dilutions, Ostwald found K_c to be constant, with a value at 25° of 1.8×10^{-5}. From the value of K_c at any temperature, then, it is possible, by solving for α, to find the degree of ionization at any dilution or at any concentration at that temperature, for $c = \frac{1}{V}$. We find

$$\alpha = \sqrt{K_cV + \frac{K_c^2V^2}{4}} - \frac{K_cV}{2},$$

where K_c is the *equilibrium, dissociation, or ionization constant, or the so-called coefficient of affinity, of the acid.*

Further than this, when K_c is known for any temperature it is possible to find α, at any dilution, in the presence of an acid or salt with an ion in common ($H^{\cdot}$ or CH_3COO'). And, just as in the case of gaseous dissociation, we always find a smaller dissociation in the presence of the products arising from an exterior source. Naturally the calculation here is similar to the other (p. 242). For example, we have

$$K_c = \frac{(c_{H^{\cdot}} + x - y)(c_{CH_3COO'} - y)}{(c_{CH_3COOH} + y)},$$

where x represents the concentration of $H^{\cdot}$ ion due to other substances, $c_{H^{\cdot}}$ and $c_{CH_3COO'}$ are the concentrations due to the acid in the absence of other substances, and y is the concentration of each ($H^{\cdot}$ and CH_3COO') lost, i.e., uniting to form un-ionized CH_3COOH, as the result of the presence of x moles of $H^{\cdot}$ ion. The concentrations of $H^{\cdot}$ and CH_3COO', now arising from the acid, are equal, then, to $(c_{H^{\cdot}} - y) = (c_{CH_3COO'} - y)$; and the ur ized acid concentration is $(c_{CH_3COOH} + y)$.

Indeed everything which we found above (pp. 241 to hold true for gaseous dissociation, with the on ception mentioned below, also holds true for the rel of ionized and un-ionized portions of a substance, c type of acetic acid, in solution. And, as a rule, th sults are simpler to calculate, for the volume chan the system is so small as to be negligible.

We can also define the *ionization constant* in similar to the definition of the *gaseous dissociation con* (p. 250). Thus by multiplying K_c for acetic acid by obtain 0.000036 as the concentration in moles per li a solution of acetic acid which would be 50% ior i.e., a solution of 1 mole of acid in 27777.5 liters of w

All organic acids when treated in this way give a stant value for the expression $\frac{\alpha^2}{(1-\alpha)V}$. This is the ference between gaseous and electrolytic dissoci equilibria, at least when the latter is for an organic *The acid, whether it be mono, di, or polybasic, a ionizes as a monobasic acid up to the dilution at* $\alpha = 0.5$. This means that, assuming the acid to i simply into the two products $H^{\cdot}$ and the negative ra (i.e., for the calculation of μ_{∞}), which may also co replaceable hydrogen, a constant is obtained so lon the ionization in this way is 50% or less. Beyond point the $H^{\cdot}$ ion, due to a breaking down of the negative ion containing replaceable hydrogen, is great enough in concentration to influence the constant, which begins to vary. Above the dilution at which $\alpha = 0.5$ the second and following replaceable hydrogens begin to appear as ion, and must be taken into account; and at infinite dilution, if it were possible to attain it, the polybasic acid would be composed of all the replaceable hydrogen as ion, together with the negative radical, without replaceable hydrogen, as the negative ion.

The calculation of the degree of ionization of dibasic acids above the dilution at which $\alpha = 0.5$ has been worked out by W. A. Smith (Zeit. f. phys. Chem., 25, 144, and 193, 1898. See also Wegscheider (Sitz. d. Akad. d. Wissenshaft, 111, 441–510, 1902), McCoy (J. Am. Chem. Soc., 30, 688–694, 1908), and Chandler (*Ibid.*, 30, 694–718, 1908).) For a tribasic acid, for example, we have the following processes taking place:

$$H_3A = H^{\cdot} + H_2A',$$
$$H_2A' = H^{\cdot} + HA'',$$
$$HA'' = H^{\cdot} + A''',$$

for which, by application of the law of mass action to each equation, we obtain

$$Kc_{H_3A} = c_{H^{\cdot}}{}' \times c_{H_2A'}, \quad K = \frac{\alpha_{,}{}^2}{(1-\alpha_{,})V_{,}};$$

$$k_2 c_{H_2A'} = c_{H^{\cdot}}{}'' \times c_{HA''}, \quad k_2 = \frac{\alpha_{,,}{}^2}{(1-\alpha_{,,})V_{,,}};$$

$$k_3 c_{HA'} = c_{H^{\cdot}}{}''' \times c_{A'''}, \quad k_3 = \frac{\alpha_{,,,}{}^2}{(1-\alpha_{,,,})V_{,,,}}.$$

It is to be noted here that the concentration of the complex ion in each reaction is the same as that in the equation below it; e.g., $c_{H_2A'}$ in 1 and 2, and $c_{HA''}$ in 2 and 3. The value $V_{,}$ is the number of liters containing 1 mole of H_3A; $V_{,,}$ that containing 1 mole of H_2A', found from the previous equation; and $V_{,,,}$ that containing 1 mole of HA, as calculated from the second equation.

Up to the dilution at which $\alpha = 0.5$ the constants k_2 and k_3 are so small that in general they have no effect on the concentration of $H^{\cdot}$ ion, which is practically equal to $c_{H^{\cdot}}'$. Above that point the value of $H^{\cdot}$ at any dilution must be taken as equal to $c_{H^{\cdot}}' + c_{H^{\cdot}}'' + c_{H^{\cdot}}'''$.

The values of the constants k_2 and k_3, and the concentrations $c_{H^{\cdot}}''$ and $c_{H^{\cdot}}'''$, can be obtained by observing the catalytic action of the acid salts, for example NaH_2A and Na_2HA, upon sugar at 100° or methyl acetate (p. 285). In these cases, also, we should have the relations given above for k_2 and k_3, and experiment has shown this to be the case. Since the mono and disodium salts of a tribasic acid increase in ionization approximately proportional to the volume, the concentration of $H^{\cdot}$ in acid salts is almost independent of the dilution. In other words, since we have $k_2 = \frac{c''_{H^{\cdot}} \times c_{HA''}}{c_{H_2A'}}$, and $c_{H_2A'}$ is approximately constant in moles *per liter*, c''_{H} from a mono- or di-sodium salt of a tribasic acid must also remain constant.

For citric acid (tribasic) the following values at 25° were determined by Smith (l.c.):

$$K = 82.0 \times 10^{-5},$$
$$k_2 = 3.2 \times 10^{-5},$$
$$k_3 = 0.07 \times 10^{-5}.$$

From these values the actual concentration of $H^{\cdot}$ ion can be calculated at any dilution; and it will be found that the second hydrogen, indeed, has little effect until the amount of H_2A' is greater than one-half the total concentration.

A few ionization constants are given below in Table

TABLE XIII.

IONIZATION CONSTANTS OF ORGANIC ACIDS AT 25° C.

	$K \times 10^5$		$K \times 10^5$
Propionic	1.34	Malic	39.5
Isobutyric	1.44	Fumaric	93
Capronic	1.45	Tartaric	97
Butyric	1.49	Salicylic	102
Valerianic	1.61	Orthophthalic	121
Acetic	1.80	Monochloracetic	155
Camphoric	2.25	Malonic	158
Anisic	3.20	Maleic	1170
Phenylacrylic	3.55	Dichloracetic	5140
Succinic	6.65	Oxalic	10060 (±)*
Lactic	13.8	Trichloracetic	121000 (±)*
Glycollic	15.2		
Formic	21.4		

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* These two acids are so largely dissociated that a small error in α affects K to a large degree. For a list containing a very large number of other acids see Zeit. f. phys. Chem., 3, 418–20, 1889, or Kohlrausch and Holborn, Leitvermögen der Elektrolyte, pp. 176–193.

XIII; they all refer to the first hydrogen, i.e., are equal to K_c in the above set of formulas.

The value of K_c at 18° for a few other acids, some of which are inorganic, but characterized by their small ionization, and by obeying the law of mass action, are given by Walker and Cormack (Trans. Chem. Soc., 77, 8, 1900), the value of acetic acid being given for comparison.

Name.	$K \times 10^{10}$	Per Cent Ionization in a 0.1 Molar Solution.
Acetic acid (25°), CH_3COO'—$H^{\cdot}$	1,800,000	1.3
Carbonic acid, $H^{\cdot}$—HCO_3'	3,040	0.174
$H^{\cdot}$—CO_3''	0.6*	....
Hydrogen sulphide, $H^{\cdot}$—HS'	570	0.075
Boric acid, $H^{\cdot}$—H_2BO_3'	17	0.01[illegible]
Hydrocyanic acid, $H^{\cdot}$—CN'	13	0.01[illegible]
Phenol, $H^{\cdot}$—C_2H_5O'	1.3	0.00[illegible]7

The constants for the ionization of the second $H^{\cdot}$ ion of some dibasic acids, according to the scheme

$$c''_{H^{\cdot}} \times c_{A''} = k_{2HA'},$$

as found by Chandler (l. c.) are given in the following table:

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* McCoy, Am. Chem. Jour., 29, 455, 1903.

Acids.	10^6k_2.	Acids.	10^6k_2.
Oxalic	41	*m*-phthalic	27
Malonic	2.0	Camphoric	14
Succinic	2.2	Itaconic	2.2
Glutaric	3.4	Maleic	0.20
Suberic	3.7	Fumaric	22.0
Pimelic	4.4	Monobromsuccinic	25
Azelaic	3.3	Dibromsuccinic	1540
o-phthalic	3.1		

These constants were determined by aid of the coefficient of partition between two, immiscible solvents, the H_2A, alone being distributed. (McCoy, Chandler, l. c.) If P is the coefficient of partition, as found for the pure H_2A, then the molecular concentration of H_2A in the water layer, for equal volumes of the two solvents, will be $\frac{1}{2}P$ times the equivalent concentration of H_2A in the other layer, where P is the coefficient of partition, i.e., $\frac{c_1}{c_2}$.

In a mixture containing the dibasic acid, partly neutralized, the following conditions must be fulfilled at equilibrium:

(*a*) $$c_{H'}\times c_{HA'}=kc_{H_2A}$$

and

(*b*) $$c_{H'}\times c_{A''}=k_2c_{HA'}.$$

Here the term $c_{H^{\cdot}}$, contrary to the usage in the above formulas, denotes the *total* concentration of $H^{\cdot}$ ion in the

By combination of (*a*) and (*b*) we obtain

$$(c)\qquad \frac{c^2_{\mathrm{HA'}}}{c_{\mathrm{H_2A}}\times c_{\mathrm{A''}}}=\frac{K}{k_2},$$

from which, if $c_{\mathrm{H_2A}}$, $c_{\mathrm{A''}}$, and $c_{\mathrm{HA'}}$ can be determined we can calculate k_2 from the known value of k, as found for the acid at dilutions at which α is less than 50%.

If α_1 and α_2 are the degrees of ionization respectively of the acid and neutral salts, we shall have, as close approximations,

$$(d)\qquad c_{\mathrm{HA'}}=\alpha_1(\Sigma c_{\mathrm{NaHA}}),$$

and

$$(e)\qquad c_{\mathrm{A''}}=\alpha_2(\Sigma c_{\mathrm{Na_2A}}),$$

where the sign Σ denotes the *total* quantity, in moles per liter, of the substance present.

As the solution is electrically neutral, we may write

$$(f)\qquad c_{\mathrm{Na^{\cdot}}}+c_{\mathrm{H'}}=c_{\mathrm{HA'}}+2c_{\mathrm{A''}},$$

($2c_{\mathrm{A''}}$ because we must have the same number of equivalents on each side, and there are $2c_{\mathrm{A''}}$ equivalents for each $c_{\mathrm{A''}}$ present); and if we designate by m the total sodium present we shall have

$$(g)\qquad c_{\mathrm{NaHA}}+2c_{\mathrm{Na_2A}}+c_{\mathrm{Na^{\cdot}}}=m$$

($2c_{\mathrm{Na_2A}}$ for $c_{\mathrm{Na_2A}}$ represent only one-half the total Na as $\mathrm{Na_2A}$ present).

Calling the total hydrogen, except that present as H_2A, in the water solution C, i.e., C equals the equivalent acid concentration of the water layer, less P times the equivalent acid concentration in the other layer (this is equal to the H_2A in the water layer), we have

$$\Sigma c_{\mathrm{NaHA}} + c_{\mathrm{H}^\cdot} = C. \tag{h}$$

From (*d*) and (*e*), then, we have

$$c_{\mathrm{HA}'} = \alpha_1 (C - c_{\mathrm{H}^\cdot}), \tag{i}$$

and from (*a*) and (*i*)

$$c_{\mathrm{HA}'} = \frac{\alpha_1 C}{2} + \sqrt{\left(\frac{\alpha_1 C}{2}\right)^2 - K\alpha_1 c_{\mathrm{H_2A}}}. \tag{j}$$

When $c_{\mathrm{H}^\cdot}$ is small compared to C, i.e., for weak acids, (*i*) becomes

$$c_{\mathrm{HA}'} = \alpha_1 C \text{ nearly.} \tag{k}$$

To which (*j*) also reduces when $K\alpha_1 c_{\mathrm{H_2A}}$ is very small compared to $\left(\frac{\alpha_1 C}{2}\right)^2$.

From (*f*) and (*g*)

$$\Sigma c_{\mathrm{NaHA}} + 2\Sigma c_{\mathrm{Na_2A}} - c_{\mathrm{H}} = m, \tag{l}$$

hence (*d*), (*e*), and (*l*) give

$$\frac{c_{\mathrm{HA}'}}{\alpha_1} + \frac{2c_{\mathrm{A}''}}{\alpha^2} - c_{\mathrm{H}^\cdot} = m \tag{m}$$

and (*i*) and (*m*),

$$(n) \qquad c_{A''} = \alpha_2\left[\frac{m+C}{2} - \frac{c_{HA'}}{\alpha_1}\right],$$

which if $c_{HA'} = \alpha_1 C$, (*k*) becomes

$$(o) \qquad c_{A''} = \alpha_2\left(\frac{m-C}{2}\right).$$

Equations (*j*) and (*n*), here, must be used for highly ionized acids, like oxalic and dibromsuccinic, but the simplified forms (*k*) and (*o*) may be used without appreciable error for the weaker acids like succinic.

Substituting these values in equation (*c*), knowing *K* it is possible to find k_2 which can then be used as abov (p. 308).

An example will perhaps make the above calculati more readily understood. The partition coefficient (of succinic acid between water and ether was found follows: 40 cc. of the water layer required 27.96 of *n*/10 Ba(OH)$_2$; while 40 cc. of the ether layer, af evaporation of the ether and re-solution of the acid water, required 3.78 cc. of the same solution of Ba(OH The apparent coefficient of partition, therefore, 27.96/3.78 = 7.40, but this must be corrected, since p of the acid in the water layer is ionized, while that the ether is not. The aqueous layer was 4.28% ioniz as calculated from its concentration, 0.0349 molar, a the known ionization constant, *K*, is 66.5×10^{-6}. T true coefficient of partition, then, is $7.40(1-0.0428) = 7.08$. Another aqueous solution of 0.1362 normal, and hence 2.19% ionized, gave for the coefficient $7.16(1-0.0219) = 7.00$. The mean of these, 7.04, is the true coefficient of partition, independent of concentration.

To find the value of the ionization constant of the second hydrogen $\left(\text{i.e., } k_2 = \frac{c_{H^\cdot} \times c_{A''}}{c_{HA'}}\right)$ 20 cc. of 0.2 molar succinic acid and 20 cc. of 0.25 normal sodium hydroxide were mixed with 50 cc. of ether, and water added until the water layer measured 50.42 cc. The sodium concentration, m, here is $\frac{20 \times 0.25}{50.42} = 0.09916$. 20 cc. of the water layer required 11.66 cc. of $n/10$ $Ba(OH)_2$; 40 cc. of the ether solution required 6.11 cc. of $n/100$ $Ba(OH)_2$. From these results it follows that the equivalent acid concentration of the water layer is 0.05830, and that of the ether layer 0.001528. Therefore $C = 0.0583 - (7.04 \times 0.001528) = 0.04754$. If $\alpha_1 = 0.80$ and $\alpha_2 = 0.70$, then $c_{HA'} = \alpha_1 C = 0.03803$ and $c_{A''} = 0.5\alpha_2(m-C) = 0.01807$, while $c_{H_2A} = 0.5 \times 7.04 \times 0.001528 = 0.00538$.

We have then from (c), since these are the quantities existing in the water layer, and in equilibrium,

$$\frac{K}{k_2} = \frac{c_{HA'}{}^2}{c_{H_2A} \times c_{A''}} = 14.8.$$

A series of such determinations gives a mean value of $\frac{K}{k_2} = 15.4$, hence since $K = 0.0000665$, $k_2 = 0.0000043$.

In the case of the addition of a salt with an ion in common to an organic acid (p. 301) the following will be seen at once to be true. If the degree of dissociation of a salt, with an ion in common with an acid, is d, and n is the number of moles of salt which are present, then the equation of equilibrium of the acid will become

$$(nd+\alpha)\alpha=K_cV(1-\alpha).$$

For very weak acids we can generalize this as follows: α, the degree of dissociation of the acid, is very small in presence of the salt, so that α in comparison to 1 and nd may be neglected. Since d for salts is almost independent of the dilution, we have

$$n\alpha=K_cV,$$

$$\alpha=\frac{K_cV}{n};$$

i.e., *the dissociation of a weak acid in presence of one of its salts is approximately inversely proportional to the amount of the salt.*

The case of the partition of a base between two acids depends to a certain extent upon their ionization constants. This partition takes place when there is not enough base present to saturate both acids. The final mixture consists of water, dissociated and undissociated salt, and the dissociated and undissociated portions of the acids. The equilibrium is the same as that which would be attained by the mixture of the salt of the one acid with the other acid. The affinity of each acid for the base will depend upon the percentage of free H˙ ion which it possesses, i.e., the one containing the larger quantity will unite with the larger amount of the base.

For weak acids it is possible to formulate a general law regarding the partition and the ionization constants. In this case α is so small that it may be neglected in $1-\alpha$; hence we have

$$K_cV=\alpha^2,$$

$$\alpha=\sqrt{K_cV}.$$

And for two acids at the same dilution

$$\sqrt{K_c} : \alpha :: \sqrt{K_c'} : \alpha',$$

or

$$\frac{\alpha}{\alpha'}=\frac{\sqrt{K_c}}{\sqrt{K_c'}}.$$

The coefficient of partition of two acids, then, is proportionate to the ratio of their degrees of dissociation at the given volume, or for WEAK *acids to* $\frac{\sqrt{K_c}}{\sqrt{K_c'}}$.

This coefficient of partition is independent of the nature of the base and depends only upon the two acids.

For the partition of an acid between two bases the coefficient will depend only upon the two bases. If α is the degree of dissociation of the one base and α' that of the other, we shall have for them when weak, just as for acids,

$$\frac{\alpha}{\alpha'}=\frac{\sqrt{K_c}}{\sqrt{K'}},$$

and the same generalization holds true.

In order that a base may be divided equally between two acids it is necessary that they be isohydric, i.e., it is necessary that

$$KC=kc.$$

An example of isohydric solutions, i.e., two which contain the same concentration of $H^{\cdot}$ ion, is acetic acid at a dilution of 8 liters and hydrochloric acid at one of 667 liters. These two solutions may be mixed in all proportions without any change in the dissociation resulting. When mixed in equal volumes, if treated with a small amount of base, equal amounts of chloride and acetate will be formed.

That these solutions may be mixed in all proportions without changing their degree of ionization may be shown in the following way; Let C and c represent the un-ionized portions, and C_H, C_2, c_H, and c_2 represent the ionized portions, where C_2 and c_2 are for different elements. We have then

$$kc = c_H c_2,$$

$$KC = C_H C_2.$$

If the volume v of the first solution be mixed with V of the second, the concentrations of the un-ionized portions, and of the unlike ions C, c, C_2, and c_2 become

$$\frac{Cv}{V+v}, \quad \frac{cv}{V+v}, \quad \frac{C_2 V}{V+v}, \quad \text{and} \quad \frac{c_2 v}{V+v},$$

while the concentration of the common H˙ ion becomes

$$\frac{C_H V + c_H v}{V+v}.$$

By application of the law of mass action, to the mixture then, we have

$$kc = \frac{C_H V + c_H V}{V+v} c_2 \quad \text{and} \quad KC = C_2 \frac{C_H V + c_H v}{V+v}.$$

But these four k equations are only satisfied when $C_H = c_H$; i.e., no displacement of the dissociation occurs by the mixing of iso-hydric solutions.

All these conclusions hold also for the organic bases, as well as some of the inorganic ones. The *ionization constants* for these are found from the relation

$$K_c = \frac{c_{M^{\cdot}} \times c_{OH'}}{c_{MOH}},$$

where M˙ is the positive and *OH′* the negative ion. The value of *K* for a few bases is given below:

Urea,	(40°.2)	$K = 0.0037 \times 10^{-11}$
Acetamide,	(40°.2)	0.0033×10^{-11}
Acetanilide,	(40°.2)	0.0044×10^{-11}
Aniline,	(25°)	5.4×10^{-10}
p-Toluidine,	(40°.2)	20.7×10^{-10}
m-Nitraniline,	(40°.2)	4×10^{-13}
p- "	(40°.2)	1×10^{-13}
o- "	(40°.2)	0.01×10^{-13}
Ammonium hydrate, $NH_4^{\cdot} - OH'$	(25°)	23×10^{-6}
Methylamine,	(25°)	5×10^{-7}
Dimethalamine,	(25°)	0.074×10^{-5}
Trimethylamine,	(25°)	0.0074×10^{-5}
Propylamine,	(25°)	0.047×10^{-5}
Isopropylamine,	(25°)	0.053×10^{-5}
Isobutylamine,	(25°)	0.034×10^{-5}

The equation on page 301 has also been used to de- termine the concentration of an ion in the solution adde to a substance obeying the law of mass action, and wit very good results. Thus, starting with acetic aci knowing the concentration of H˙ ion, and adding sodiu acetate, we can find the concentration of CH_3CO ion in the salt. In this case the new concentration H˙ ion can be determined from the speed of inversio of sugar; and, by solving the equation for the amou of CH_3COO' added, we can find the dissociation of th salt solution added.

This same process may also be carried out with othe systems, mentioned below, and by it it is possible t determine the concentration of any one kind of ion. A mentioned above, the ionization has been found to be sensibly the same, by whatever method it may be determined.

An interesting relation has been found by Osaka (Coll. Sci. and Eng. Mem., Kyoto, 1, 103, 1905; 3, 205–210, 1907) to exist between the concentration of H˙ ion (or OH˙ ion) in a weak acid (or weak base) when it is 50% neutralized by a strong base (or strong acid). If the acid (or base) is very slightly ionized and the salt practically completely ionized, we have

$$HA+\tfrac{1}{2}Na^{\cdot}+\tfrac{1}{2}OH'=\tfrac{1}{2}H_2O+\tfrac{1}{2}HA+\tfrac{1}{2}Na^{\cdot}+\tfrac{1}{2}A'.$$

Hence in

$$c_{H^{\cdot}}=\frac{Kc_{HA}}{c_A}$$

inspection shows that $c_A=c_{HA}$, and

$$c_{H^{\cdot}}=K_{acid}.$$

The concentration of H˙ ion in a weak acid 50% neutralized by a strong base is equal to the ionization constant of the acid, provided the salt is practically completely ionized.

For a weak base, 50% neutralized by a strong acid, we find in the same way

$$c_{OH'}=K_{base}.$$

If an equimolecular mixture of two acids is 50%

neutralized by a strong base and the salts remain practically completely ionized, we shall have

$$HA+HB+Na^{\cdot}+OH'=H_2O+xHA+(1-x)HB$$
$$+(1-x)A'+xB^{\cdot}+Na^{\cdot}$$

and

$$c_{H^{\cdot}}=\frac{K_1c_{HA}}{c_{A'}}=\frac{K_2c_{HB}}{c_{B^{\cdot}}};$$

but $c_{HA}=c_{B'}$, and $c_{HB}=c_{A'}$. Hence

$$c^2_{H^{\cdot}}=K_1K_2;\quad c_{H^{\cdot}}=\sqrt{K_1K_2}.$$

The concentration of $H^{\cdot}$ ion in an equimolecular mixture of two weak acids, which is 50% *neutralized by a strong base is equal to the square root of the product of the two ionization constants.*

It is also possible, in the same way, to find $c_{H^{\cdot}}$ (or $c_{OH'}$) when the acid (or base) is 1/3, 1/4, or 1/5, etc., neutralized by a strong base (strong acid).

72. Acids, bases, and salts which are ionized to a considerable extent. Empirical dilution laws.—The application of the law of mass action (the Ostwald dilution law) to the above so-called strong electrolytes does not lead to a constant value for K when the ionization is taken from the conductivity ratio $\frac{\mu_v}{\mu_\infty}$. *As in general the degree of dissociation is found to be the same by all of the possible methods, our only conclusion at present is* *that the law of mass action cannot be applied to the equilibrium of un-ionized and ionized portions in such solutions as these.* Although this is true with regard to very soluble salts, there is a quantitative relation, which we shall develop below, holding for the ionized portions of difficultly soluble substances, when the un-ionized portion is retained constant.

The only known case of a dissociating and very soluble salt to which the law of mass action may be applied, i.e., the only exception to the above conclusion, is cæsium nitrate, when α is determined by the freezing-point method. And this is not true for α as determined by the other methods. In other words, in this case the freezing-point results point to a different degree of ionization than any other method. The results for cæsium nitrate as determined by Biltz (Zeit. f. phys. Chem., 40, 218, 1902) by the freezing-point and conductivity methods are given below.

BY DEPRESSION OF THE FREEZING-POINT.

c (Moles per Liter).	V (Liters per Mole).	Depression.	α (Obs.).	$K=\frac{\alpha^2}{(1-\alpha)V}$.
0.00766	130.7	0.028	0.98	0.33
0.01940	51.6	0.070	0.95	0.35
0.04648	21.6	0.164	0.907	[0.41]
0.09884	10.2	0.331	0.810	0.34
0.1421	7.09	0.460	0.750	0.32
0.2100	4.81	0.662	0.704	0.35
0.2987	3.385	0.907	0.641	0.34
0.3861	2.62	1.125	0.575	[0.30]
0.4339	2.33	1.267	0.578	0.34

Average K, excluding values in brackets, $=0.34$

BY CONDUCTIVITY, $\mu_\infty = 147$.

V (Liters per Mole).	μ_v.	$K = \frac{\alpha^2}{(1-\alpha)V}$.
1024	146.4	....
512	144.7	....
256	141.9	....
128	139.3	0.14
64	138.3	0.23
32	134.2	0.30
16	128.1	0.37
8	120.9	0.47
4	111.9	0.61

Biltz attributes the failure of the law of mass action, as applied to strong electrolytes, to a hydration of the substance—i.e., to a chemical reaction between the substance and the solvent—which would remove active solvent from the solution, so that it would be really more concentrated than it appears to be. Just why the solution of cæsium nitrate in water should give a constant value for K when α is determined by the freezing-point method, while for conductivity it fails to do so, is unknown and thus far nothing but assumption has been possible. It is to be remembered, however, that this value of K, although giving, when solved for α, the ionization according to the freezing-point method, does not give the value as determined by any other method, so that too much stress is not to be laid upon it, especially in face of the fact that the law cannot be applied to any other strong electrolyte by any method of determining α. It would seem more probable that some secondary action takes place in the freezing which is absent in all other cases, so that in this one case the freezing-point result is incorrect. This, of course, may not be true, but at the present time, in the absence of any indication of such a result for other substances, it is decidedly the most reasonable and logical one. In other words, then, so far as we know at present, in all cases but this the conductivity leads to the true value for α, so that it is but reasonable, until further evidence is at hand to assume it be correct here, and attribute the case above to some abnormality not yet encountered with other substances.

It has also been observed that picric acid and nitric acid both give constants for the Ostwald dilution law when α is determined by the partition of the acid between two immiscible solvents (water-benzene and water-ether), although the values of α as found by conductivity fail to lead to a constant. See Rothmund and Drucker (Zeit. f. phys. Chem., 46, 827, 1903) and Bogdan (Zeit. f. Elektrochem., 11, 824, 1905, and 12, 489–493, 1906).

Although the Ostwald dilution law fails utterly to hold in other cases for the equilibrium between the ionized and un-ionized portions of strong electrolytes, however determined, certain other empirical dilution laws have been found which allow us to find the respective amounts at any dilution. Thus Rudolphi (Zeit. f. phys. Chem., 17, 385, 1895) found a dilution law which gives a constant value between certain limits for such solutions as do not follow the Ostwald dilution law. This law is

$$\frac{\alpha^2}{(1-\alpha)\sqrt{V}}=\text{constant},$$

where the value of the constant is approximately the same for analogous substances. van't Hoff (Zeit. f. phys. Chem., 18, 300, 1895) altered this to the form

$$\frac{\alpha^3}{(1-\alpha)^2 V}=\text{constant},$$

which holds even better than Rudolphi's. Simplified this relation is

$$\frac{c_i^3}{c_s^2}=\text{constant},$$

i.e., *the cube of the concentration of ions divided by the square of the undissociated portion is a constant.*

Writing the Ostwald dilution law in this form we obtain (*for binary electrolytes*)

$$K=\frac{c_i^2}{c_s},$$

while this empirical relation (in either form) remains the same for binary or ternary substances; in other words, is independent of the number of ions formed from one mole of the substance.

Some values found by use of van't Hoff's equation are given below. The value of k by the Ostwald dilution law will be found to vary considerably, while k_H is quite constant, i.e., within the experimental error.

$AgNO_3$ 25°.

$V = 16$	$\alpha = 0.8283$	$k_H = 1.11$
$= 32$	$= 0.8748$	$= 1.16$
$= 64$	$= 0.8993$	$= 1.06$
$= 128$	$= 0.9262$	$= 1.07$
$= 256$	$= 0.9467$	$= 1.08$
$= 512$	$= 0.9619$	$= 1.09$

Bancroft (Zeit. f. phys. Chem., 31, 188, 1899) proposes a dilution law of the form

$$\text{constant} = \frac{C_i^n}{C_s},$$

in which the constant and n are functions of the nature of the electrolyte. Although this relationship is as yet unknown, Bancroft suggests that we may sometime find a relation of the form

$$n = 2 - f\ (\text{constant})$$

(where f (*constant*) varies between zero and a value approximating one-half) which will reconcile the Ostwald dilution law, holding only for organic acids and bases, and in which $n=2$, with this form in which n varies between the values 1.36 and 1.5. For KCl at 18° we have the relation $\frac{C_i^{1.36}}{C_s}=2.63$, which holds in a very remarkable way between the volumes 0.3 and 10,000 liters, as will be seen by referring to the results in the following table:

KCl AT 18°.

$$\frac{C_i^{1.36}}{C_s}=2.63.$$

a		V
Obs.	Calc.	
0.987	0.987	10000
0.984	0.983	5000
0.978	0.976	2000
0.973	0.970	1000
0.965	0.962	500
0.950	0.948	200
0.934	0.934	100
0.915	0.917	50
0.902	0.906	33.3
0.883	0.892	20
0.853	0.864	10
0.821	0.834	5
0.803	0.813	3.3
0.780	0.786	2
0.748	0.745	1
0.706	0.700	0.5
0.673	0.672	0.3

For other substances the relation $\frac{C_i^n}{C_s}$ is not so satisfactory or constant. Noyes (J. Am. Chem. Soc., 26, 168, 1904) has determined the degree of ionization, $\frac{\mu_v}{\mu_\infty}$, for the chlorides of potassium and sodium at various temperatures and finds a constant value for the ratio $\frac{1-\alpha}{c^{\frac{1}{3}}}$: *that is, the fraction of salt un-ionized is directly proportional to the cube root of the concentration, or the concentration of un-ionized substance,* $(1-\alpha)c$, *is directly proportional to the* 4/3 *power of the total concentration,* c, *of salt.* The degrees of ionization of potassium and sodium chlorides were found to be nearly identical (the extreme variation being 2%) at all temperatures and dilutions. In a 0.1 molar solution the dissociation has approximately the following values:

18°	84%	281°	67%
140°	79%	306°	60%
218°	74%		

The values of $K'=\frac{1-\alpha}{c^{\frac{1}{3}}}$ are as follows:

	18°	140°	218°	281°	306°
NaCl.	0.366	0.448	0.573	0.745	0.877
KCl.	0.321	0.468	0.577	0.713	0.853

Some of the observed facts as to the ionization of strong electrolytes, as summarized by Noyes (Technology Quarterly, 17, 307, 1904; and also in Carnegie Publication No. 63, 1907) are as follows:

The form of the concentration function is independent of the number of ions into which the mole of salt dissociates. Instead of being proportional for di-ionic, tri-ionic, and tetra-ionic to the square, cube, or fourth power of the concentration of the ions, the undissociated portion is approximately proportional to the 3/2 power of that concentration, whatever may be the type of salt.

The conductivity and freezing-point depression of a mixture of salts having an ion in common are those calculated under the assumption that the degree of ionization of each salt is that which it would have if present alone at such an equivalent concentration that the concentration of either of its ions were equal to the sum of the equivalent concentrations of all the positive or negative ions present in the mixture. Suppose that a mixed solution is 0.1 molar with respect to sodium chloride and 0.2 molar with respect to sodium sulphate, and that it is 0 18 molar with reference to the positive or negative ions of these salts. The principle then requires that the ionization of either of these salts in the mixture be the same as it is in water alone when its ionic concentration is 0.18 molar. This has been proven conclusively for many mixtures.

The decrease of ionization with increasing concentration is roughly constant in the case of different salts of the same type.

The un-ionized fraction of any definite molal concentration is roughly proportional to the product of the

.ences of the two ions in the case of salts of different ɔes.*

From these facts, together with others, Noyes (l.c.) ncludes that the form of union represented by the ı-ionized portion of a substance differs essentially from 'dinary chemical combination, it being so much less timate that the ions still exhibit their characteristic :operties, in so far as these are not dependent upon eir existence as separate aggregates. In other words, e law of mass action is inapplicable to the relation :tween ionized and un-ionized portions as they exist strong electrolytes, and hence this is not to be conlered as a *simple chemical equilibrium*, for which, we know, the law of mass action appears to hold ;idly.

73. **Heat of ionization.**—By the van't Hoff equation . 269) it is possible to calculate the heat of ionization a substance, provided we know the degrees of ionizan, at any one dilution, at two different temperatures. ıis is true not only for those substances which follow ɜ Ostwald dilution law, but for all others as well, accord-; to Arrhenius (Zeit. f. phys. Chem., 4, 96, 1889, and 339, 1892). For binary electrolytes we have then

$$q_v = \frac{R \times 2.306\left(\log\frac{\alpha_1{}^2}{(1-\alpha_1)V_1}\log\frac{\alpha^2}{(1-\alpha)V}\right)TT'}{T-T'}$$

$$K_{c'} = \frac{\alpha_1{}^2}{(1-\alpha_1)V'} \text{ and } K_c = \frac{\alpha^2}{(1-\alpha)V},$$

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* Other generalizations of this kind will be found in Chapter IX ler Electrical Conduct*ivity*.

where the values of K_c *are for the same dilution and represent the change of ionization*, even though the values are not the same as at other dilutions. *q is then the heat liberated when a mole of substance ionizes in solution, at a temperature equal to the mean of those at which $K_{c'}$ and K_c are calculated.* It will be observed here that these values differ from those calculated from the table given on page 234, for these refer to the heat of formation of the ions from substance already in solution, while those refer to the compound process of solution and ionization, i.e., the difference in energy between the ionized state and the solid or gaseous state. Some of the results as found by Arrhenius are given below, the unit being the small calorie.

Heats of Ionization.

Substance.	Temperature.	Calories.
Acetic acid	35°	386
	21°.5	− 28
Propionic acid	35°	557
	21°.5	183
Butyric acid	35°	935
	21°.5	427
Phosphoric acid	35°	2458
	21°.5	2103
Hydrofluoric acid	33°	3549
Potassium chloride	35°	362
“ iodide	“	916
“ bromide	“	425
Sodium chloride	“	454
“ hydrate	“	1292
“ acetate	“	391
Hydrochloric acid	“	1080

The ionization of a substance in solution thus usually takes place with an evolution of heat.

AT EVOLVED BY THE COMPLETION OF THE IONIZATION (1 mole in 200 moles of water).

Substance.	Temperature.	Calories.
Potassium bromide	35°	58
" iodide	"	132
" chloride	"	56
Sodium hydrate	"	180
" chloride	"	81
Hydrochloric acid	"	136
Hydrofluoric acid	33°	3304
Phosphoric acid	21°.5	1682

Above (p. 232) it was noted that the heat of neutraliza-
n of an acid by a base is made up of the heat of asso-
.tion of $H^{\cdot}$ and OH' ions ($137K$) plus the heat of
sociation of the salt found plus the sum of the heats
olved in the completion of the ionizations of the acid
d base. We are now in the position to test this relation
antitatively, for we can now calculate the heats of
nization of the acid, bases, and salts. This relation
n be expressed mathematically in the following simple
rm:

$$ {}_{\text{neut.}} = 13700 - w_3(1 - \alpha_3) + w_2(1 - \alpha_2) + w_1(1 - \alpha_1) \text{ cals.,} $$

ere the figures 1, 2, and 3 refer respectively to acid,
e, and salt, and $w_3(1 - \alpha_3)$, the heat evolved by the
sociation of the salt, is subtracted because its *negative*
ue is equal to the heat of *association* required in the
ation. The table given below is self-explanatory,
d certainly shows conclusively that, as was mentioned
fore, *the value of the heat of neutralization of an acid*

by a base cannot be considered as indicative of the strength of the acid. The two latter are relatively weak acids and yet they give rise to the greatest amount of heat.

HEAT OF NEUTRALIZATION OF ACIDS WITH NaOH.

(1 mole of acid + 1 mole of NaOH + 400 moles of H_2O.)

	At 35°.	At 21.5.	
	Calc.	Calc.	Obs.
HCl	12867	13447	13740
HBr	12945	13525	13750
HNO_3	12970	13550	13680
CH_3COOH	13094	13263	13400
C_2H_5COOH	13390	13598	13480
$CHCl_2COOH$	14491	14930	14830
H_3PO_4	14720	14959	14830
HF*	16184	16320	16270

We have found thus that the van't Hoff equation can be used for the calculation of the heats of *dissociation* or *ionization*, and also (pp. 275-276) for the heats of *solution*, when the substance is either completely ionized or completely un-ionized. So far, however, it has been found impossible to calculate the heats of *solution* of substances which are partly ionized.

74. Solubility or ionic product. — Although, as we have seen, the law of mass action cannot in general be applied to the equilibrium of the ionized and un-ionized portions of a substance in solution (except to organic acid and bases), it can be applied with considerable accuracy to a very large number of saturated solutions.

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* For data as to the ionization of HF, see Deussen, Zeit. f. anorg. Chem., 44, 408, 1905.

An example of such an equilibrium is a saturated solution of silver chloride, which is found to be practically completely ionized according to the scheme

$$\mathrm{AgCl} = \mathrm{Ag}^{\cdot} + \mathrm{Cl}'.$$

Applying the law of mass action to this we obtain

$$Kc = c_1 c_2, \quad \text{or} \quad K = \frac{\alpha^2}{(1-\alpha)V},$$

when c is the concentration of un-ionized AgCl, c_1 that of the $\mathrm{Ag}^{\cdot}$ ion, and c_2 that of the Cl' ion. Since the solution is saturated, the value of c at any temperature must remain constant, for if the solution were unsaturated, solid would dissolve, if supersaturated, solid would precipitate. We have then, at any one temperature, in a saturated solution of silver chloride, the relation

$$Kc = \text{constant} = c_1 c_2;$$

i.e., *in a saturated solution of a binary electrolyte (of this kind) the product of the concentrations of the ions must remain constant, with unchanged temperature.*

Expressing this in a more general form, we have for the reaction

$$nA \rightleftarrows n_1 A_1 + n_2 A_2$$

in a saturated solution,

$$(25) \qquad c_1^{n_1} c_2^{n_2} = \text{constant} = s,$$

where s was called by Ostwald *the solubility product of the substance.* This solubility product, which may be defined as *the greatest possible product of the concentrations of the constituent ions according to* (25) *which can exist at any one temperature*, is of paramount importance in analytical chemistry, *for a precipitate* (*when due to an ionic reaction, and most of them can be shown to be due to this*) *is always and only formed when its solubility product is exceeded.* This, of course, presupposes that no supersaturation phenomenon is possible; if it is, then the *metastable limit* (p. 143) must first be exceeded. Stieglitz (Jour. Am. Chem. Soc., 30, 946–954, 1908) points out in this connection that even if the un-ionized portion does not remain constant, it is an empirical fact that the *product of the concentrations of the ions* (25), *the solubility product, is a constant*, and may be considered as empirical.

Just as we found a decrease in the dissociation of a gas or an organic acid, by the addition of one of the products of dissociation from an exterior source, so here the addition of a substance with an ion in common causes the formation and separation in the solid state of the un-ionized substance. In other words, the term s still retains its constant value, and consequently the constituent ions of the substance unite to form more of the un-ionized portion, which, since the solution is already saturated with it, separates out as solid. This has been found to be true by experiment, *but only true for those substances which are difficultly soluble.* The effect may be observed most easily by dissolving the difficultly soluble substance in a solution of the salt with an ion in common; but it can also be attained by adding to the saturated water solution of the substance a strong solution of the salt, when a precipitation of the substance, usually in the crystalline state, will be observed. Thus if we add to one portion of a saturated solution of silver acetate a strong solution of sodium acetate containing x moles of CH_3COO' ion, and the same amount of a solution of silver nitrate containing x moles of $Ag^{\cdot}$ to the liter to another equal portion, we observe an equal precipitation of solid silver acetate in the two solutions.

Although all this is true, as far as the precipitation is concerned for all saturated solutions, it is only for the difficultly soluble substances that the quantitative relations are found to hold.

The examples below will serve to show how the solubility product of a substance can be found, and how when once found can be employed to foresee the solubility of the substance in a solution already containing a common ion.

Silver bromate is soluble at 25° to the extent of 0.0081 moles per liter. Assuming the ionization in this state to be practically complete, and it certainly is nearly so, the concentration of the ions $Ag^{\cdot}$ and BrO_3' will be the same, and equal each to 0.0081 mole per liter. The solubility product at this temperature, then, will be

$$(0.0081)(0.0081) = s_{AgBrO_3}.$$

The solubility in a solution of silver nitrate containing 0.1 mole of $Ag^{\cdot}$ ion (or in potassium bromate containing 0.1 mole of BrO_3' ion) can be found by aid of the relation

$$(0.0081)^2 = (0.0081 + .1 - y)(0.0081 - y),$$

and is equal to $(0.0081 - y)$, for that is the concentration of $Ag^{\cdot}$ and BrO_3' ions now existing in the solution, and coming from the salt; the amount 0.1 of one being due to the other salt, and y being the $AgBrO_3$ remaining undissolved owing to the presence of this 0.1 mole of $Ag^{\cdot}$ or BrO_3'.

This is true for all binary salts when they can be assumed to be completely ionized, or practically so.

Where the substance dissociates into more than tw ions and can be assumed to be completely ionized, th relation is quite similar. Suppose the salt to dissociat according to the scheme

$$MA_3 \rightleftarrows M^{\cdots} + 3A'.$$

As solubility product we shall have, if c is the solubility of the completely ionized salt MA_3,

$$c \times (3c)^3 = s_{MA_3},$$

or

$$c_{M^{\cdots}} \times c^3_{A'} = s_{MA_3},$$

for we must have three times the number of moles per liter of A' as we have of $M^{\cdots}$ according to the chemical equation, i.e.,

$$c = c_{M^{\cdots}} \quad \text{and} \quad 3c = c_{A'}.$$

In case of solution in the presence of 0.1 mole of one of the ions, we have, then,

[illegible]

or

[illegible]

from which it is [illegible] that the [illegible] of [illegible] addition is not the same for the [illegible] 3. The decrease in the solubility [illegible] the M[illegible] are not [illegible]

In the case the substance is not completely ionized, the solubility product is not so directly related to the solubility of the substance as in the above cases, i.e. to the square in one case and twenty-seven times the fourth power in the other. Consider the case of uric acid, which, at 25°, is soluble to 0.0001506 mole per liter, and is ionized in that condition to 9.5% into $H^{\cdot}$ and the negative radical which we shall designate as U'. The solubility product here is naturally

$$(0.0001506\times 0.095)\ (0.0001506\times 0.095)$$
$$=s_{HU}=K_{HU}(0.0001506\times 0.905),$$

where we use the s_{HU}, the product of the two constants at this temperature, i.e., K_{HU} times 0.0001506×0.905.

The solubility of uric acid in a molar solution of hydrochloric acid, for which $\alpha=0.78$ (i.e., $H^{\cdot}=0.78$, $Cl'=0.78$), is to be found in the following way:

$$(0.0001506\times 0.095+0.78-x)(0.0001506\times 0.095-x)$$
$$=(0.0001506\times 0.095)^2,$$

where $(0.0001506\times 0.095-x)$ represents the present concentration of $H^{\cdot}$ and U' from the uric acid, and its total solubility in the hydrochloric acid solution is $(0.0001506\times 0.905)+(0.0001506\times 0.095-x)$, i.e., is equal to the sum of that which is un-ionized and that which is ionized.

Just as for organic acids in general, an infinite excess of one of the ions will cause the ionization of the substance to become zero. *It is to be observed here, however, that this excess will only* cause the solubility *to become zero* *in the case that the ionization is compete.* In the case of uric acid, an infinite amount of $H^{\cdot}$ or U' at best can only reduce the solubility by 9.5%, the remaining 90.5% being un-ionized and not affected at that temperature by any addition of substance which does not react chemically with it.

That a substance is *always* decreased in solubility by the addition of a substance with an ion in common is not true, as the well-known behavior of silver cyanide in potassium cyanide will show. In all such cases, however, the equilibrium which has previously existed is altered in some way, so that the relations are not the same. These cases are usually characterized by the formation of a complex ion, the *product* of which is exceeded. The removal of the ions to form this complex ion disturbs the equilibrium of the difficultly soluble salt; the un-ionized portion ionizes further, and its loss is replaced by the solid phase. This process continues, dissolving new salt, until equilibrium is attained, i.e., until the solubility product, whatever it may be, is just satisfied, when solution ceases. The ionization of silver potassium cyanide takes place almost completely according to the scheme

$$KAgCN_2 = K^{\cdot} + AgCN_2',$$

but it has been found by Morgan (Zeit. f. phys. Chem., 17, 513–535, 1895) that in a 0.05 molar solution we have $Ag^{\cdot}$

where the value of s, in each case, is equal to 55.5 times the value of $K_c = \frac{\alpha^2}{(1-\alpha)V}$, V being 0.0018 liter, i.e., the volume occupied by the formula weight, 18 grams, of water.

Knowing the solubility products of two substances with an ion in common, it is possible to find how much of each will dissolve when they are exposed together to the action of a solvent; and this, of course, may be expanded to three or more substances together.

Assume we have the two completely ionized, difficultly soluble salts MA and MA_1, with the ion $M^{\cdot}$ in common, and that they are dissolved simultaneously in water. Call the amount of MA which dissolves x, and the amount of MA_1 y. In the solution then we must have $x+y$ moles of $M^{\cdot}$ ion, x of A' and y of A_1'; and, if s is the solubility product of MA and s_1 that of MA_1, the relations must be

$$x(x+y)=s,$$
$$y(x+y)=s_1,$$

so that by solving the simultaneous equations we can find x and y. Naturally, if the ionization is not complete we must still represent the ionized portion by x and y, and then after finding the degree of ionization when mixed, if that is possible, we can calculate the total amount of each dissolved.

An example of this is given by dissolving thallium loride and sulphocyanate together. The solubilities water, each for itself, are $TlCl = 0.0161$ and $TlSCN$ 0.0149. Assuming complete ionization, the solu-ity products are respectively $(0.0161)^2$ and $(0.0149)^2$, d if x represents the amount of chloride and y that sulphocyanate dissolving from the mixture, we have $+y = Tl^{\cdot}$, $x = Cl'$, and $y = SCN'$, and

$$x(x+y) = (0.0161)^2,$$
$$y(x+y) = (0.0149)^2,$$

om which we find $x = 0.0118$ and $y = 0.0101$, while e values $x = 0.0119$ and $y = 0.0107$ are found by periment.

It will be observed that in the above examples, except e last, we have tacitly assumed that the dissociation the added salt, with an ion in common, is not influenced the ions of the difficultly soluble salt. As a rule this true, for the substances are so insoluble that their fect is infinitesimal; in the last example, this effect as been allowed for, however, and will show the method treating such cases.

In general, then, we can conclude for difficultly soluble lts (and for complex ions) that they are precipitated ormed) when the product of the concentrations of the ions mposing them exceeds the solubility (ionic) product.

Although this law holds in general for difficultly soluble salts, isolated cases are to be found where the un-ionized portion does not remain rigidly constant, after the addition of an ion in common; and, to a smaller extent, a slight variation is sometimes observed in the solubility product. Since these cases are very few, and are usually observed for the more soluble salts, it would seem probable that they are due to secondary reactions not yet recognized, or to others not properly accounted for.

75. **Hydrolytic dissociation. Hydrolysis.**—Hydrolysis is the process taking place in the water solution of a *salt*, which causes the solution to appear alkaline or acid, or results in a neutral equilibrium according, for example, to the scheme

$$MA + H_2O = MOH + HA.$$

If the acid formed is insoluble or un-ionized, the base being ionized, the reaction will be alkaline (OH' ion). When the base is insoluble or un-ionized, and the acid ionized, the reaction is acid ($H^{\cdot}$ ion). And finally, if both acid and base are insoluble or un-ionized, the salt will be completely transformed into base and acid, and, as there will remain no excess of either $H^{\cdot}$ or OH' ion, the reaction will be neutral. In other words, then, hydrolysis is due to the removal of either $H^{\cdot}$ or OH' ion (or both) from the water by the A' or $M^{\cdot}$ ion of the salt, to form un-ionized or insoluble substances, and this continually causes more water to ionize, i.e., to react with the salt until a state of equilibrium is attained.

Examples of this process are most common. For instance, all mercury, copper, zinc, etc., salts are acid, for an un-ionized basic substance is formed by the reaction leaving free, ionized acid; and potassium cyanide is alkaline, owing to the formation of un-ionized hydrocyanic acid and ionized potassium hydrate. The most striking example of this process, perhaps, is the precipitation of bismuth oxychloride when water is added to a hydrochloric acid solution of the chloride, but the basic acetate separation of iron is just as characteristic, although apparently not so direct.

Since we know the conditions under which insoluble or un-ionized substances will form, i.e., by the exceeding of their solubility products or analogous values, it is possible to find the conditions necessary to produce a hydrolytic dissociation, and also to find the relations governing the equilibrium finally attained as the result of the process.

We recognize at once that if the product of the concentrations of $M^{\cdot}$ and OH' ions is larger than that which can exist in pure water, un-ionized substance must form. By this formation, however, the equilibrium of $H^{\cdot}$ and OH' ions will be disturbed, and a further ionization of water must take place, until at length the ionic product is just attained. If the $H^{\cdot}$ and A' ions at this point do not unite to form un-ionized acid, the further ionization of water will be unlike what it would be in the absence of this excess of H˙ ion, for, since $c_{H^{\cdot}} \times c_{OH'}$ must at the same time be equal to s_{H_2O}, we can only have $\frac{s_{H_2O}}{c_{H^{\cdot}}}$ moles per liter of OH′ ion present, when $c_{H^{\cdot}}$ is the total concentration of H˙ ion at that time.

The process due to the formation of un-ionized or insoluble acid, when no un-ionized base is formed, or forms but slightly, is exactly analogous to the above. In both cases water is decomposed, owing to the removal of one of its ions, and the further ionization of water and formation of the insoluble or un-ionized base or acid continues until the equations for equilibrium are fulfilled.

For the sake of simplicity we shall consider separately the cases that the reaction is caused primarily by the base, primarily by the acid, or by both base and acid.

CASE I. *The formation of un-ionized or insoluble base is the direct cause of the hydrolytic dissociation, and the acid formed is largely ionized.* By definition, here, hydrolysis, which may occur according to one of the three typical equations,*

(*a*) $MA + H_2O = MOH + HA,$

(*b*) $MA_2 + 2H_2O = M(OH)_2 + 2HA,$

(*c*) $MA_3 + 3H_2O = M(OH)_3 + 3HA,$

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* The reader can calculate for himself, after studying the following pages, the changes that would be caused if the negative radical *A* were di- or trivalent. See also Hill, Trans. Chem. Soc., 89, 1273-1289, 1906.

st occur until the product—depending upon the ence of the positive ion of the salt—

$$c_{M^{\cdot}} \times c_{OH'};$$

$$c_{M^{\cdot\cdot}} \times c^2_{OH'},$$

$$c_{M^{\cdot\cdot\cdot}} \times c^3_{OH'},$$

greater than that which can exist in the absence of ionized base, for then un-ionized base must form. d the formation of base (and acid) must continue il equilibrium is established *in the solution*, i.e., until condition, for (*a*), (*b*), or (*c*),

$$\text{final } c_{M^{\cdot}} \times \text{final } c_{OH'} = K_{MOH} \times c_{MOH} \text{ formed,}$$

$$\text{final } c_{M^{\cdot\cdot}} \times (\text{final } c_{OH'})^2 = K_{M(OH)_2} \times c_{M(OH)_2} \text{ formed,}$$

$$\text{final } c_{M^{\cdot\cdot\cdot}} \times (\text{final } c_{OH'})^3 = K_{M(OH)_3} \times c_{M(OH)_3} \text{ formed,}$$

fulfilled.

In case the base formed is difficultly soluble, since the terion of equilibrium holds for the substance in solun, i.e., for a homogeneous equilibrium, the above conions would naturally simplify to the following:

$$\text{final } c_{M^{\cdot}} \times \text{final } c_{OH'} = s_{MOH},$$

$$\text{final } c_{M^{\cdot\cdot}} \times (\text{final } c_{OH'})^2 = s_{M(OH)_2},$$

$$\text{final } c_{M^{\cdot\cdot\cdot}} \times (\text{final } c_{OH'})^3 = s_{M(OH)_3},$$

the excess of un-ionized base formed separating out as a solid, leaving the concentration *in solution* constant.

In addition to the above equilibria in the solution, we must also always have the condition

$$c_{\mathrm{H}^\cdot} \times c_{\mathrm{OH}'} = s_{\mathrm{H_2O}}$$

fulfilled. Hence it is evident that the final concentration of OH′ ion can always be readily found by dividing $s_{\mathrm{H_2O}}$, at the temperature in question, by the final concentration of H· ion, which is dependent only upon the extent of the hydrolysis, i.e., of the reaction, and the ionization of the acid at the concentration to which it is formed.

If we designate by α the percentage of salt hydrolyzed, i.e., the percentage of the salt decomposed according to the chemical reaction, by d_s the ionization of the salt left, and by d_{A} the ionization of the acid, i.e., the fraction of the acid formed which remains ionized, the final concentration of M·, M··, or M··· ion, from an original concentration of salt of 1 mole in V liters, will be $\frac{d_s(1-\alpha)}{V}$, and that of the un-ionized base, which causes the reaction, will be $\frac{\alpha}{V}$. The total acid formed will be $\frac{\alpha}{V}$ for (*a*), $\frac{2\alpha}{V}$ for (*b*), and $\frac{3\alpha}{V}$ for (*c*), the concentration of H· ion being respectively $\frac{d_{\mathrm{A}}\alpha}{V}$, $\frac{2d_{\mathrm{A}}\alpha}{V}$, and $\frac{3d_{\mathrm{A}}\alpha}{V}$.

We have, then, substituting these values in the above conditions of equilibrium, when the base is not difficultly soluble,

$$\frac{d_s(1-\alpha)}{V}\frac{s_{H_2O}}{d_A\frac{\alpha}{V}}=K_{MOH}\frac{\alpha}{V},$$

$$\frac{d_s(1-\alpha)}{V}\left(\frac{s_{H_2O}}{2d_A\frac{\alpha}{V}}\right)^2=K_{M(OH)_2}\frac{\alpha}{V},$$

$$\frac{d_s(1-\alpha)}{V}\left(\frac{s_{H_2O}}{3d_A\frac{\alpha}{V}}\right)^3=K_{M(OH)_3}\frac{\alpha}{V};$$

and when the base is difficultly soluble, i.e., when the solubility product may be substituted for the product of ionization constant and un-ionized base,

$$\frac{d_s(1-\alpha)}{V}\frac{s_{H_2O}}{d_A\frac{\alpha}{V}}=s_{MOH},$$

$$\frac{d_s(1-\alpha)}{V}\left(\frac{s_{H_2O}}{2d_A\frac{\alpha}{V}}\right)^2=s_{M(OH)_2},$$

$$\frac{d_s(1-\alpha)}{V}\left(\frac{s_{H_2O}}{3d_A\frac{\alpha}{V}}\right)^3=s_{M(OH)_3}.$$

By simplification these six conditions become

$$\left.\begin{array}{ll}\dfrac{\alpha^2}{(1-\alpha)V}\cdot\dfrac{d_A}{d^s}=\dfrac{s_{H_2O}}{K_{MOH}}=K_{hyd.} & \text{when the base MOH is soluble}\\ \text{or} & \\ \dfrac{\alpha}{(1-\alpha)}\cdot\dfrac{d_A}{d^s}=\dfrac{s_{H_2O}}{s_{MOH}}=K_{hyd.} & \text{when the base MOH is difficultly soluble}\end{array}\right\}(a)$$

$$\left.\begin{array}{ll}\dfrac{4\alpha^3}{(1-\alpha)V^2}\cdot\dfrac{d_A{}^2}{d_s}=\dfrac{s^2{}_{H_2O}}{K_{M(OH)_2}}=K_{hyd.} & \text{when the base } M(OH)_2 \text{ is soluble}\\ \text{or} & \\ \dfrac{4\alpha^2}{(1-\alpha)V}\cdot\dfrac{d_A{}^2}{d_s}=\dfrac{s^2{}_{H_2O}}{s_{M(OH)_2}}=K_{hyd.} & \text{when the base } M(OH)_2 \text{ is difficultly soluble}\end{array}\right\}(b)$$

and

$$\left.\begin{array}{ll}\dfrac{27\alpha^4}{(1-\alpha)V^3}\cdot\dfrac{d_A{}^3}{d_s}=\dfrac{s^3{}_{H_2O}}{K_{M(OH)_3}}=K_{hyd.} & \text{when the base } M(OH)_2 \text{ is soluble}\\ \text{or} & \\ \dfrac{27\alpha^3}{(1-\alpha)V^2}\cdot\dfrac{d_A{}^3}{d_s}=\dfrac{s^3{}_{H_2O}}{s_{M(OH)_3}}=K_{hyd.} & \text{when the base } M(OH)_3 \text{ is difficultly soluble}\end{array}\right\}(c)$$

In other words, *the constant of a hydrolytic dissociation which is caused by the formation of base can be found from the ionic product of water and either the ionization constant or the solubility product of the base which is the cause of the hydrolytic dissociation.*

It will be observed that the variation of the hydrolytic dissociation with the dilution depends upon whether the base causing it is difficultly soluble or not.

Thus *when 1 mole of salt reacts with 1 mole of water, (a), if the base is difficultly soluble the extent of hydrolysis is independent of the dilution of the salt, while when the base is soluble the hydrolysis depends upon the dilution.* It must be remembered here, however, that even when the salt is difficultly soluble, the hydrolytic dissociation and its relation to dilution will be the same as for a soluble base up to the value that would cause a *separation of solid base.*

When the hydrolysis is small, i.e., $1-\alpha$ is practically 1, and d and d_s are also equal to 1, it will be seen that for (*a*), (*b*), and (*c*), *for a soluble base* that the hydrolytic dissociation will vary as the $\sqrt{V}$, $\sqrt[3]{V^2}$, and $\sqrt{V^3}$; while when the base is difficultly soluble the hydrolysis will be independent of the dilution for (*a*) and will vary as $\sqrt{V}$ and $\sqrt[3]{V^2}$ for (*b*) and (*c*).

CASE II. *The formation of un-ionized, or unsoluble, acid is the direct cause of the hydrolytic dissociation, and the base formed is largely ionized.* Here, by definition, hydrolysis, which may occur in one of the three forms (*a*), (*b*), and (*c*), already mentioned, according as the valence of the positive ion of the salt is mono-, di-, or trivalent, must in all cases occur when the product, *in the solution,*

$$c_{A'} \times c_{H^{\cdot}},$$

is greater than that which can exist in the absence of un-ionized acid, for then un-ionized acid must form. And the formation of acid (and base) must continue until the condition,

$$\text{final } c_{A'} \times \text{final } c_{H'} = K_{HA} \times c_{HA} \text{ formed}$$

is fulfilled. Or until the condition, when the acid is difficultly soluble,

$$\text{final } c_{A'} \times \text{final } c_{H'} = s_{HA}$$

is fulfilled.

Since the final $c_{H'}$ is equal to $\frac{s_{H_2O}}{\text{final } c_{OH'}}$, when d_B is the ionization of the amount of base formed, α is the percentage of hydrolytic dissociation, and d_s is the ionization of the salt left, we have, as before,

$$\text{final } c_{A'} = \frac{d_s(1-\alpha)}{V}, \quad \text{final } c_{OH'} = d_B\frac{\alpha}{V},$$

$$\left(\text{or } \frac{2d_B\alpha}{V} \text{ or } \frac{3d_B\alpha}{V}\right), \text{ and}$$

$$\text{final } c_{HA} = \frac{\alpha}{V}\left(\text{or } \frac{2\alpha}{V} \text{ or } \frac{3\alpha}{V}\right)$$

the conditions for (*a*), (*b*), and (*c*), when the acid is soluble, are respectively,

$$\frac{d_s(1-\alpha)}{V} \frac{s_{H_2O}}{d_B\frac{\alpha}{V}} = K_{HA} \times \frac{\alpha}{V},$$

$$\frac{d_s(1-\alpha)}{V}\frac{s_{H_2O}}{\frac{2d_B\cdot\alpha}{V}}=K_{HA}\times\frac{2\alpha}{V},$$

or

$$\frac{d_s(1-\alpha)}{V}\frac{s_{H_2O}}{\frac{3d_B\alpha}{V}}=K_{HA}\times\frac{3\alpha}{V};$$

and when the acid is difficultly soluble and its solubility product is s_{HA},

$$\frac{d_s(1-\alpha)}{V}\frac{s_{H_2O}}{\frac{d_B\alpha}{V}}=s_{HA},$$

$$\frac{d_s(1-\alpha)}{V}\frac{s_{H_2O}}{\frac{2d_B\alpha}{V}}=s_{HA},$$

or

$$\frac{d_s(1-\alpha)}{V}\frac{s_{H_2O}}{\frac{3d_B\alpha}{V}}=s_{HA}.$$

These by simplification become, for a soluble acid,

(*a*) $$\frac{\alpha^2}{(1-\alpha)V}\cdot\frac{d_B}{d_s}=\frac{s_{H_2O}}{K_{HA}}=K_{hyd.},$$

(*b*) $$\frac{4\alpha^2}{(1-\alpha)V}\cdot\frac{d_B}{d_s}=\frac{s_{H_2O}}{K_{HA}}=K_{hyd.},$$

and

(*c*) $$\frac{9\alpha^2}{(1-\alpha)V}\cdot\frac{d_B}{d_s}=\frac{s_{H_2O}}{K_{HA}}=K_{hyd.}.$$

and for *difficultly soluble acids* to

(*a*) $$\frac{\alpha}{1-\alpha}\cdot\frac{d_B}{d_s}=\frac{s_{H_2O}}{s_{HA}}=K_{hyd.},$$

(*b*) $$\frac{2\alpha}{(1-\alpha)}\cdot\frac{d_B}{d_s}=\frac{s_{H_2O}}{s_{HA}}=K_{hyd.},$$

and

(*c*) $$\frac{3\alpha}{(1-\alpha)}\cdot\frac{d_B}{d_s}=\frac{s_{H_2O}}{s_{HA}}=K_{hyd.},$$

where in all cases the extent of the hydrolytic dissociation is independent of the dilution of the salt.

In case the reaction is $M_2A+2H_2O=2MOH+H_2A$, where H_2A is slightly ionized or slightly soluble, and MOH is largely ionized the same result will be found as (*b*) under Case 1, if we substitute d_B for d_A, and K_{H_2A} or s_{H_2A} for $K_{M(OH)_2}$ and $s_{M(OH)_2}$, ie., it will be

$$\frac{4\alpha^3}{(1-\alpha)V^2}\cdot\frac{d_B{}^2}{d_s}=\frac{s^2{}_{H_2O}}{K_{H_2A}}=K_{hyd.}\text{ for a soluble acid,}$$

and

$$\frac{4\alpha^2}{(1-\alpha)V}\cdot\frac{d_B{}^2}{d_s}=\frac{s^2{}_{H_2O}}{s_{H_2A}}=K_{hyd.}\text{ for a difficultly soluble acid.}$$

CASE III. *The formation of both un-ionized acid and un-ionized base causes the hydrolytic dissociation, both* *are but slightly ionized.* This case falls under one or the other of those above, according as the base or acid has the smaller ionization constant or solubility product. Although the mechanism of the reaction is the same here as above, the final result is quite different.

Assume that K_{HA} is smaller than K_{MOH}. Since the final $c_{OH'}$ is equal to $\frac{K_{MOH}c_{MOH}}{c_M}$, and if both MOH and HA are slightly ionized we shall have, practically, $c_{MOH} = c_{HA} = \frac{\alpha}{V}$ and $c_{M'} = c_{A'} = \frac{d_s(1-\alpha)}{V}$. Consequently just as with (*a*), Case II, we must have

$$\frac{d_s(1-\alpha)}{V}\cdot\frac{s_{H_2O}}{\dfrac{K_{MOH}\frac{\alpha}{V}}{\dfrac{d_s(1-\alpha)}{V}}} = K_{HA}\times\frac{\alpha}{V},$$

which when simplified gives

$$\frac{\alpha^2}{(1-\alpha)^2}\cdot\frac{1}{d_s^2} = \frac{s_{H_2O}}{K_{HA}\times K_{MOH}} = K_{hyd.},$$

the hydrolytic dissociation of a salt reacting with 1 *mole of water to form a slightly ionized acid and a slightly ionized base is independent of the dilution, so long as the salt is completely ionized; and the constant of hydrolytic dissociation is equal to the ionic product for water* *divided by the product of the ionization constants of the acid and base.*

When the salt reacts with 2 or more moles of water the hydrolytic dissociation is also independent of the dilution, so long as the salt is completely ionized. The value of the constant for 2 moles (*b*) can be readily shown to be

$$\frac{4\alpha^3}{(1-\alpha)^3}\cdot\frac{1}{d_s^3}=\frac{s^2{}_{H_2O}}{K^2{}_{HA}\times K_{M(OH)_2}},$$

and for other forms of the reaction it may also be found without difficulty.

Here it is not difficult to see that if both base and acid are difficultly soluble, the reaction will be complete at all dilutions, and the same result will be obtained if one is insoluble and the other but slightly ionized. The latter case is to be observed in the well-known basic acetate separation, where the ferric hydroxide is difficultly soluble and the already small ionization of the acetic acid formed is depressed by the presence of sodium acetate.

It will be seen from the above that from the law of mass action it is possible to find an expression for the equilibrium that must be established as the result of a hydrolytic dissociation, whether taking place with one or more moles of water, and forming un-ionized or insoluble base and acid, or both. The first form of the expression is the more valuable for many purposes, though the latter ($K_{\text{hyd.}}$) is useful as connecting directly the degree of hydrolytic dissociation and the dilution of the salt solution. The reader is advised to pay especial attention to the first form throughout, and especially to its very simple and logical derivation, for from that, if necessary, he can always derive the second form, instead of attempting to burden his memory with it.

Naturally, just as on pages 250 and 302, so long as d_s, d_A, or d_B, are equal to 1, we may define K, the hydrolytic constant, for a reaction involving 1 mole of water as equal to 1/2 the concentration in moles per liter at which the salt is 50% hydrolyzed. And it is also evident that knowing the constant for hydrolytic dissociation, we can calculate the degree of hydrolysis for any dilution, so long as d_s, d_B, or d_A are equal to 1.

From hydrolytic dissociation, determined according to the methods given later, it is possible for us to find the ionization constant or solubility product of the acid or base causing it, or when that is already known, to find the ionic product of water.

What is the ionic product of water at 25°? A 0.1 molar solution of sodium acetate is 0.008% hydrolyzed. Here we may regard the sodium acetate as practically completely ionized, as will also be the sodium hydroxide formed, and we know that the constant of ionization of acetic acid at 25° is 0.000018. It is evident here, from the reaction

$$CH_3COO' + Na^{\cdot} + H_2O$$
$$= xNa^{\cdot} + xOH' + (1-x)CH_3COO' + xCH_3COOH,$$

where $x = 0.1 \times 0.00008$, that

$$c_{CH_3COOH} = c_{OH'} = 0.00008 \times 0.1 = 0.000008$$

mole per liter at equilibrium, and since

$$c_{CH_3COO'} = 0.1 - (0.00008 \times 0.1) = 0.1, \text{ practically,}$$

and

$$0.000018 \times c_{CH_3COOH} = c_{H^{\cdot}} \times c_{CH_3COO'},$$

$$c_{H^{\cdot}} = \frac{0.000018 \times 0.000008}{0.1} = 1.44 \times 10^{-9},$$

and

$$1.44 \times 10^{-9} \times 0.000008 = c_{H^{\cdot}} \times c_{OH'} = 1.21 \times 10^{-14},$$

i.e., the ionization of water (where $H^{\cdot} = OH'$) is such that $H^{\cdot} = OH' = \sqrt{1.21 \times 10^{-14}}$ at 25°.

What is the hydrolysis of a 0.1 molar solution of potassium cyanide (assuming $d_s = 1$)? K for HCN is 13×10^{-10}, and $s_{H_2O} = (0.91 \times 10^{-7})^2$ at 25°.

$$K_{\text{hyd.}} = \frac{\alpha^2}{(1-\alpha)V} = \frac{(0.91 \times 10^{-7})^2}{13 \times 10^{-10}},$$

from which, since d_B is plainly 1 and $V = 10$, we find $\alpha = 0.00798$; i.e., KCN$n/10$ is 0.8% hydrolyzed forming OH' and HCN.

n such a case as the above, where α is so small that α is practically equal to 1, the equation reduces to $=\alpha^2$, or $\alpha=\sqrt{K_{\text{hyd.}}V}$, just as on page 313. In er words, for the same substance the hydrolytic sociation, being small, is proportional to $\sqrt{V}$ or to

t will be noted in all cases of hydrolytic dissociation t since the ionization of water *increases* with increased perature, up to a certain point, page 339, and the ization of dissolved substances *decreases* with in-ased temperature, *the degree of hydrolytic dissociation reases with the temperature.* Thus for acetic acid, $_8=18.3\times10^{-6}$, $K_{100^\circ}=11.4\times10^{-6}$, $K_{156^\circ}=5.6\times10^{-6}$, l $K_{218^\circ}=1.9\times10^{-6}$, while for ammonium hydrate $_{3^\circ}=17.1\times10^{-6}$, $K_{100^\circ}=14\times10^{-6}$ and $K_{156^\circ}=6.6\times10^{-6}$. mparing these with the values s_{H_2O} for the various peratures (page 339) shows that the hydrolysis of monium acetate (Case III) must increase decidedly h the temperature. And the same is true for all er cases.

n the table below are given the values of $\frac{\alpha^2}{(1-\alpha)V}$ for ious equilibria in which but 1 mole of water reacts h the substance, the base causing the hydrolysis ase I).

HYDROLYSIS OF HYDROCHLORIDES AT 25°.

Base.	Per Cent Hydrolysis at $V=32$.	$\frac{a^2}{(1-a)V}$	Ionization Constant of Free Base.
Aniline	2.7	2.25×10^{-5}	5.3×10^{-10}
o-Toluidine	7.0	1.62×10^{-4}	7.3×10^{-12}
m- "	3.6	4.10×10^{-5}	2.9×10^{-10}
p- "	1.8	1.05×10^{-5}	1.13×10^{-9}
o-Nitroaniline	98.6	2.1	5.6×10^{-15}
m- "	26.6	3.01×10^{-3}	4.0×10^{-12}
p- "	79.6	9.58×10^{-2}	1.24×10^{-13}
Aminoazobenzene	18.1	1.25×10^{-3}	9.5×10^{-10}
Urea	....	0.781	1.5×10^{-14}

An example of Case I, where the salt reacts with 2 moles of water, is the hydrolysis of aluminum chloride according to the reaction,

$$AlCl_3+2H_2O=Al(OH)_2Cl+2HCl,$$

This has been investigated by Kullgren (Om metallsalters hydrolys, page 108. Dissertation. Stockholm, 1904). The following results will show how well this equilibrium follows the above law, and how it is possible to find the ionization constant by aid of the hydrolytic dissociation, knowing the ionic product for water at that temperature.

HYDROLYSIS OF $AlCl_3$ AT 100° C.

$$AlCl_3+2H_2O=Al(OH)_2Cl+2H^{\cdot}+2Cl'.$$

V	a	d_A	d_S	$\frac{a^3}{(1-a)V^2}$	$K_{hyd.}=\frac{a^3}{(1-a)V^2}\cdot\frac{d^3_A}{d_S}$
96	0.1488	0.966	0.76	420×10^{-9}	516×10^{-9}
384	0.3629	0.977	0.85	509×10^{-9}	571×10^{-9}
1536	0.7142	1	0.91	541×10^{-9}	594×10^{-9}
			Average,		$K_{hyd.}=560\times 10^{-9}$

The concentrations of base in the three cases are 0.00155, 0.000945 and 0.000465, respectively, the acid concentrations being twice these values. The average value of

$K_{\text{hyd.}}$ in the last column may be used to determine $K_{\text{Al(OH)}_2\text{Cl}}$, for $\frac{s^2_{\text{H}_2\text{O}}}{K_{\text{Al(OH)}_2\text{Cl}}} = 4\frac{\alpha^3}{(1-\alpha)V^2} \cdot \frac{d_{\text{A}}{}^2}{d_{\text{S}}}$. We obtain in this way (according to Kullgren) the value $K_{\text{Al(OH)}_2\text{Cl}} = 2.33 \times 10^{-19}$, where the ionization, presumably, gives $\text{AlCl}^{\cdot\cdot}$ and $2\text{OH}'$.

$\text{Tl(NO}_3)_3$, according to Spencer and Abegg (Zeit. f. anorg. Chem., 44, 397, 1905), seems to react directly with 3 moles of water, Tl(OH)_3 having a solubility equal to $10^{-13.58}$ moles per liter, i.e., $s = 10^{-52.896}$ and so is an illustration of Case I, where the formation of insoluble M(OH)_3 is the primary cause of the hydrolysis. Unfortunately the actual degrees of hydrolysis have not been determined, but simply the fact that the reaction goes in this way.

Examples of Case II, where the hydrolytic dissociation is due primarily to the acid are the hydrolysis of potassium cyanide, sodium acetate, sodium carbonate, the barium salt of hydroxyazobenzene, etc.

PERCENTAGE OF HYDROLYSIS.

Basalt of hydroxyazobenzene.

V	t	%	$K_{\text{hyd.}}$.
50	25°	1.10	$24. \times 10^{-7}$
	Sodium Acetate.		
548	156°	0.87	—
593	218°	4.34	—
118	218°	1.12	—
15.6	218°	0.29	—
10	25°	0.008	—

Sodium Carbonate.

V	t	%	$K_{\text{hyd.}}$
5	25°	2.12	—
10	25°	3.17	—
20	25°	4.87	—
40	25°	7.10	—
	Potassium Phenate.		
10	25°	3.05	—
50	71°	6.65	—
	Borax.		
32	25°	0.92	—

Examples of Case III, where both acid and base are but slightly ionized, and α for the reaction with 1 mole of water is independent of the dilution, so long as the ionization of the salt is complete, are solutions of ammonium acetate, ammonium borate, aniline acetate.

Aniline Acetate.

V	t	α	d_s
39.32	15°	0.457	0.869
195.9		0.468	0.95
39.32	25°	0.513	0.873
195.9		0.523	0.953
39.32	40°	0.590	0.878
195.9		0.595	0.959

Ammonium Borate.

				$K_{\text{hyd.}}=\left(\frac{\alpha}{1-\alpha}\cdot\frac{1}{d_s}\right)^2=\frac{s_{HO}}{K_{HA}K_{MOH}}$
46.46	15°	0.390	0.880	0.528
92.92		0.394	0.944	0.508
46.46	25°	0.458	0.885	0.912
92.92		0.462	0.919	0.875
46.46	40°	0.556	0.894	1.961
92.92		0.560	0.956	1.883

Ammonium Acetate.

t	α	d_8
100°	0.046	—
100°	0.048	—
156°	0.1797	—
156°	0.1860	—
218°	0.526	—
218°	0.532	—
306°	0.913	—
306°	0.915	—

must now consider, very briefly, the methods by
h the degree of hydrolytic dissociation can be experi-
ally determined. It is obvious from what has
dy been said, that the determination of the concen-
n of any one of the reacting constituents, together
the chemical reaction, will give us a complete view
e equilibrium.

e general methods so far used for this purpose
s follows:

) The free acid (H˙) or free base (OH′) is measured
bservations of the velocity of the inversion of sugar
00°, or the hydrolysis of esters, as was described
e (page 286) (Walker, Zeit. f. phys. Chem., 4, 319,
; Shields, *ibid.*, 12, 167, 1893).

) The determination of the ionized portion by means
nductivity observations (see Chapter IX).

r details as to these methods see Ley (Zeit. f. phys.
m., 30, 193, 1899), Goodwin, *ibid.*, 21, 1, 1896,

Kullgren (l. c.), Lundén (Jour. chim. Phys., 5, 145, and 574, 1907), and Noyes (Carnegie Pub. No. 63, 1907).

When one of the active constituents is colored, the reaction may also be followed by aid of spectro-photometric observations, as shown by Moore (Phys. Rev., 12, 151–176, 1900), but, naturally, this method is much limited in its applicability.

Other methods are based on the determination of the concentration of H˙ by electromotive force measurements. (Denham, Trans. Chem. Soc., 93, 41, 1908) on the mobility of the ions (Denison and Steele, Trans. Chem. Soc., 89–90, 999, 1368, 1906); on the distillation of systems where the hydrolysis is due to a volatile constituent (Veley, Trans. Chem. Soc., 87, 26, 1905); Hill, *ibid.*, 90, 1273, 1906; Naumann and Rücker, J. f. prakt. Chem., 74, 249, 1906; and Naumann and Müller, *ibid.*, 74, 218, 1906).

One method, which can be used for salts of weak acids with strong bases, or salts of weak bases with strong acids, has been suggested by Farmer (Trans. Chem. Soc., 79, 863, 1901, and *ibid.*, 85, 1713, 1904), which owing to the importance of the principle involved, is briefly considered below. The method is based upon the coefficient of distribution of a substance between water and another solvent, ether. (p. 268).

Let the coefficient of partition of the distributable base (of the same molecular weight in both solvents), for example, between water and ether, be $P=\frac{w_w}{w_e}$, where w_w and w_e are the weights of the base *in grams per cc.* of the layers water and ether at equilibrium. After thus determining P, by experiment, we are to use it to find the concentration in moles per liter in the water layer, and consequently must proceed as follows: Assume the reaction

$$MA+H_2O=MOH+HA,$$

where the base is very slightly ionized and soluble in both solvents, while the salt and acid are practically completely ionized and soluble only in the water layer. It is evident from $P=\frac{w_w}{w_e}$ that

$$w_w=Pw_e$$

and

$$c_w=\frac{1000Pw_e}{M},$$

for $1000\frac{w_w}{M}$ is equal to c_w the concentration of the base MOH in moles per liter of the water layer.

If the water layer measures 1000 cc., and the ether layer x cc., then the total moles of base in the two layer system must be $\frac{1000Pw_e}{M}+\frac{xw_e}{M}$. This, however, according to the above chemical reaction, must also be equal to the total acid in the system, which is contained only in the water layer. We have, then,

$$\text{Acid in water layer}=\frac{1000Pw_e}{M}+\frac{xw_e}{M}.$$

$$\text{Base in water layer} = c_w = \frac{1000 P w_e}{M}.$$

$$\text{Salt, un-hydrolyzed, in water layer} = c - \left(\frac{1000 P w_e}{M} + \frac{x w_e}{M}\right),$$

where c is the original concentration in the water solution of the salt, in moles per liter.

The hydrolytic constant for the salt MA must be, therefore, since these three substances are in equilibrium. in the water layer,

$$K_{\text{hyd.}} = \frac{\text{acid} \times \text{base}}{\text{salt}} = \frac{\left(\frac{1000 P w_e}{M} + \frac{x w_e}{M}\right)\left(\frac{1000 P w_e}{M}\right)}{c - \left(\frac{1000 P w_e}{M} + \frac{x w_e}{M}\right)},$$

and from this, knowing the dilution of the salt V in $\frac{\alpha^2}{(1-\alpha)V} = K_{\text{hyd.}}$, we can solve for α, the hydrolytic dissociation of the salt MA, in the equation

$$\alpha = \sqrt{K_{\text{hyd.}} V + \frac{K^2_{\text{hyd.}} V^2}{4}} - \frac{K_{\text{hyd.}} V}{2}.$$

As an illustration of this method we may take the hydrolysis of aniline hydrochloride, where the hydrolysis is caused by the formation of free un-ionized aniline which distributes between the water and ether. After shaking (at 25°) 1 liter of water containing 0.09969 moles of aniline hydrochloride with 59 cc. of ether we find 0.001156 gram of aniline ($M = 93$) per cc. of ether, i.e., $\frac{59 \times 0.001156}{93} = 0.000733$ mole of aniline in the 59 cc. of the ether layer. The amount of aniline in the 1000 cc. of the water layer, then, is $\frac{1000\frac{1}{10.1}\times 0.001156}{93}$ $=0.00123$, for P was previously found to be $\frac{1}{10.1}$, i.e., there is always at 25°, 10.1 times as much aniline in 1 cc. of the ether layer as in 1 cc. of the water layer. The total amount of free base in the *system*, then, is, $0.00123+0.000733=0.00196$, and this is equal to the amount of free acid in the *water layer*, while the final un-hydrolyzed salt in the water layer is $0.09969-0.00196=0.09773$, for the original concentration of salt was 0.09969 mole per liter. We have then in the water layer

$$K_{\text{hyd.}}=\frac{0.00123\times 0.00196}{0.09773}=0.0000247,$$

from which for this practically $n/10$ solution, the hydrolytic dissociation,

$$\alpha=0.0156 \quad \text{or} \quad 1.56\%.$$

This method is also to be used for reactions involving two or more moles of water when appropriately altered; and is also applicable to those reactions producing un-ionized acid, where that is distributed between the two solvents (see Farmer, l. c.).

76. Determination of the ionization constant from observations of increased solubility.—A very ingenious and accurate method for the determination of the ionization constant of an acid or a base, from its increased solubility in a base or an acid, with a known ionization constant, is given by Lowenherz (Zeit. f. phys. Che 15, 385, 1898). Either the acid or base to be de mined must be difficultly soluble in water, i.e., just th conditions are advantageous which in the usual meth are sources of trouble.

The general form of the equilibrium arising by neutralization of an acid with a base may be writ as follows:

$$HA + MOH = aHA + bMOH + cH_2O + dMA + eH^{\cdot} + fA' + gM^{\cdot} + hOH'.$$

Calling the total amount of acid present ΣA, and t total base ΣM, we have the following conditions existi at equilibrium:

(1) $A' = \Sigma A - HA - MA.$

(2) $A' = M^{\cdot} + H^{\cdot} - OH'$. The sum of the positive io is equal to the sum of the negative.

(3) $M^{\cdot} = \Sigma M - MA - MOH.$

(4) $M^{\cdot} = A' + OH' - H^{\cdot}.$

(5) $H^{\cdot} = \dfrac{K_{acid} HA}{A'}.$

(6) $H^{\cdot} = \dfrac{S_{H_2O}}{OH'}.$

(7) $OH' = \dfrac{K_{base} MOH}{M^{\cdot}}$

(8) $OH' = \dfrac{S_{H_2O}}{H^{\cdot}}.$

(9) $MA = (1 - \alpha_{MA})$ total MA.

(10) $MOH = (1 - \alpha_{MOH})$ total MOH.

(10a) MOH, when difficultly soluble is the same as in a saturated water solution.

(11) $H_2O =$ total MA.

(12) $HA = (1 - \alpha_{HA})$ total HA.

(12a) HA, when difficultly soluble is the same as in a saturated water solution.

The solubility of a difficultly soluble acid, for example, will be greater in a solution of a [illegible] for the reaction causes the [illegible] the acid and the [illegible] the un-ionized [illegible] The difference [illegible] directly the amount [illegible] very simple examples, however, will probably do more to show the principles involved than pages of explanations.

Assume we have an acid, soluble to 0.001 mole per liter, the constant of ionization of which is unknown, which is soluble to 0.003 mole per liter in a 0.1 molar solution of the base MOH. The base is 90% ionized, and the salt which is formed, has a value of α equal to 98% at this dilution. What is the constant of ionization of the acid?

Here we must find $K_{HA}=\frac{c_{H^\cdot}\times c_{A'}}{c_{HA}}$. Since the difference in the two solubilities is 0.002, the amount of water and the total salt formed are each equal to 0.002 mole per liter. We have, then,

$$\begin{aligned}
MA &= (1-\alpha)\ (\text{total } MA)\\
&= (1-0.98)(0.002).\\
M^\cdot &= M^\cdot \text{ of } MOH - \text{loss of } M^\cdot \text{ as } MA\\
&= 0.9(0.1)-(0.002)(1-0.98).\\
OH' &= OH' \text{ of } MOH - \text{loss of } OH' \text{ as } H_2O\\
&= 0.9(0.1)-(0.002).
\end{aligned}$$

$$\begin{aligned}
H^\cdot &= \frac{S_{H_2O}}{OH'}\\
&= \frac{(1.09\times 10^{-7})^2}{0.9\ (0.1)-(0.002)}.\\
A' &= H^\cdot + M^\cdot - OH'
\end{aligned}$$

$$=\frac{(1.09\times10^{-7})^2}{0.9(0.1)-(0.002)}+[0.9\,(0.1)-(0.002)(1-0.98)]$$
$$-[0.9\,(0.1)-(0.002)]$$
$$=\frac{(1.09\times10^{-7})^2}{0.088}+0.00196.$$

$$\mathrm{HA}=\Sigma\mathrm{A}-\mathrm{A}'-\mathrm{MA}$$
$$=0.003-\left[\frac{(1.09\times10^{-7})^2}{0.c88}+0.00196\right]$$
$$-(1-0.98)(0.002).$$

And since

$$K=\frac{c_{\mathrm{H}^{\cdot}}\times c_{\mathrm{A}'}}{c_{\mathrm{HA}}},$$

we can find its value by substituting the values given above, i.e., $\mathrm{H}^{\cdot}$, A', and HA.

Proceeding in this way, and only in this way, we can find the concentrations of the various constituents at equilibrium.

The sequence of determination is somewhat different when the base is difficultly soluble and K_{base} is unknown, an acid solution with a known degree of ionization serving as solvent.

Assume a base, which is soluble to 0.001 mole per liter, to be soluble in a 0.1 molar solution of acid ($\alpha=0.90$) to the extent 0.003 mole per liter, the salt being ionized to 0.98%. What is $K\left(=\frac{c_{\mathrm{M}^{\cdot}}\times c_{\mathrm{OH}'}}{c_{\mathrm{MOH}}}\right)$ for the base?

Here again

$$\mathrm{MA}=(0.002)(1-0.98),$$

but now we must first determine A' instead of $M^{\cdot}$ as above, i.e.,

$$A' = A' \text{ of HA} - \text{loss of A as MA}$$
$$= 0.9(0.1) - (0.002)(1 - 0.98).$$
$$H^{\cdot} = H^{\cdot} \text{ of HA} - \text{loss of } H^{\cdot} \text{ as } H_2O$$
$$= 0.9(0.1) - (0.002).$$

$$OH' = \frac{s_{H_2O}}{H^{\cdot}}$$
$$= \frac{(1.09 \times 10^{-7})^2}{0.9(0.1) - (0.002)}.$$
$$M^{\cdot} = A' + OH' - H^{\cdot}$$
$$= [0.9(0.1) - (0.002)(1 - 0.98)] + \frac{(1.09 \times 10^{-7})^2}{0.9(0.1) - (0.002)}$$
$$- [0.9(0.1) - (0.002)].$$
$$= 0.00196 + \frac{(1.09 \times 10^{-7})^2}{0.088}.$$

$$MOH = \Sigma M - M^{\cdot} - MA$$
$$= 0.003 - \left[0.00196 + \frac{(1.09 \times 10^{-7})^2}{0.088}\right]$$
$$-(0.002)(1 - 0.98)$$

and

$$K_{\text{base}} = \frac{c_{M^{\cdot}} \times c_{OH'}}{c_{MOH}},$$

the values of which are above, viz , $M^{\cdot}$, OH', and MOH.

In case the acid is dibasic, or the metal of the base is divalent, the appropriate changes may be made in the above formulas without difficulty.

In all cases, however, it is necessary to have the solvent id or base) considerably more concentrated than the solved substance (base or acid).

7. **Other ionic equilibria.**—In order that the importe of the things we have just studied may be more rly realized, we shall now consider very briefly their lication to a few other questions of general chemical rest. Since the states of equilibrium which we most n encounter in our daily experience are those comed of ionized substances, and since those composed of ionized substances are comparatively simple and easy determine, we shall restrict ourselves here to the conration of systems containing ionized substances.

he simpler cases of ionic equilibria, i.e., those exist- in simple electrolytes, have already been considered ve. We found then that the law of mass action bles us to foresee the equilibrium in systems comed of organic acids or bases, of substances which difficultly soluble, or of those of which the ionization very slight. But for other systems, characterized by arge degree of ionization, the law of mass action is parently inapplicable, and must be replaced by certain pirical relations.

We also found complications to arise in these equiria, produced by the further dissociation at higher utions of one of the two ions observed at lower dilu-ns. This is the case with the poly-basic organic acids, which, up to the dilution at which $\alpha = 0.5$, behave as though monobasic, only showing their real basicity above this dilution. Even in such a case, however, the process can be followed or foreseen by the law of mass action, each form of ionization leading to a constant ratio of the concentrations of the constituents. An analogous case with a strong electrolyte is that of sulphuric acid, which ionizes in two stages, as follows:

$$H_2SO_4 = H^{\cdot} + HSO_4,$$
$$HSO_4' = H^{\cdot} + SO_4''.$$

Here, however, we cannot follow the process by the law of mass action, and the first stage is only to be observed in concentrated solutions. Indeed, at and above a dilution of 1 mole in 5 liters no trace of the HSO_4' ion can be detected, and a dilution of 1 mole in 1000-2000 liters shows practically complete ionization into $2H^{\cdot}$ and SO_4''. The behavior of salts of the type of $BaCl_2$ is similar to this; and in general we may say that *the more dilute the solution the smaller the amount of a complex ion present.* (See Luther, Z. f. Elektrochem., 13, 294, 1907; and Noyes, Carnegie Publication, 239-281, No. 63.)

All these cases of equilibrium are comparatively simple, however, for all the ionized matter present arises from the one original substance with which we start. The cases we are now to consider, i.e., those equilibria resulting from the reaction of two or more substances, are somewhat more complicated experimentally, for the ionized matter may be due to several substances, but theoretically they are to be treated just as the others.

Before considering the specific cases of equilibrium which have been observed, it will be well to review very briefly the various methods for the determination of ionization and molecular weight in solution, in order that the physical-chemical analysis of such systems may be quite clear. In those electrolytes ionizing into two portions measurements of the electrical conductivity or freezing-point depression give all the necessary information, i.e., of ionized, as well as of un-ionized matter. This is also true when three ions are formed completely. When one of the three ions is formed to a smaller extent than the others, however, as is the case with the second $H^{\cdot}$ ion of dibasic organic acids, some other method, in addition to the ones above, must be employed in order to show its concentration. As the equilibrium becomes still more complicated, i.e., contains other ionized and un-ionized substances, still other methods must also be employed. In short, the physical-chemical analysis can only be accomplished by a combination of two or more of these methods.

Starting with a given solution containing various ions and un-ionized substances, by the application of all or some of the following methods, we can, of course, ascertain the concentration of each of the constituents if this be necessary. As a matter of fact, however, this is usually unnecessary, for, as will be seen from page 330, knowing the values of certain ones, those of the others may be found by aid of the chemical and physical-chemical relations.

The electrical conductivity of a solution gives directly *the total concentration of the ions which it contains;* while the freezing-point, boiling-point, vapor pressure, or osmotic pressure give the *total number of moles per liter, i.e., of ionized plus un-ionized matter.* These are the general methods applicable to all kinds of ionized or un-ionized matter and their application to an unknown solution is obvious. In addition to these, however, there are certain other special methods, applicable to certain kinds of ions and un-ionized matter, which enable us to make a more detailed analysis of the solution. For example, by the depression of the solubility of a substance with an ion in common, the concentration of that ion in the solution employed as the solvent may be calculated, and with great accuracy. The *nature* of the ions in general may be determined by migration experiments, i.e., by observing the changes in concentration due to the passage of the electric current; and by aid of electromotive force measurements the individual *concentrations* of many kinds of ions may be accurately calculated. For details as to these methods see Chapter IX. Concentrations of ionized hydrogen may also be found from the speed of the inversion of cane sugar, using a weak, known solution of an acid as a standard; and OH′ ion can be determined from the speed of saponification of an ester, a known and weak solution of a strong base being used as a standard. And, finally, un-ionized aggregates can be determined by partition or distribution experiments, i.e., by finding the concentration of the substance in another, immiscible solvent, after this has been shaken with the original solution. And this, it is to be remembered, is not restricted to any one un-ionized substance, for even when several are present together they behave as if they were alone, and so can be determined.

By these methods, then, it is possible for us to find the concentrations of the various substances present at equilibrium, both ionized and un-ionized, and thus to define exactly the conditions necessary and sufficient for the retention of that state.

As was said above, we are now to consider the equilibria resulting from the reaction of two or more substances, but, since a chemical reaction in ionized systems depends largely upon the formation of un-ionized or difficultly soluble substances, it will be seen at once that the law of mass action is applicable to these systems. For such cases where it is inapplicable we have no guiding principle at present, but these are few, so far as we know, and at any rate are of lesser importance in ordinary work.

One of the first questions arising in qualitative analysis is—what occurs when the precipitation of $Mg(OH)_2$ by ammonium hydrate is prevented by the presence of ammonium chloride? The older theory of this influence assumed the formation of a complex salt $(MgCl_4)(NH_4)_2$, which is not decomposed by ammonium hydrate; while according to the new theory it is due to the fact that the ionization of the ammonium hydrate is so decreased by the presence of the $NH_4^{\cdot}$ ion of the chloride that the solubility product of $Mg(OH)_2$ cannot be exceeded.

This question was first investigated by Lovén (Zeit. f. anorg. Chem., 37, 327, 1896). If the action is due to the driving back of the ionization of NH_4OH by the $NH_4^{\cdot}$ of NH_4Cl, the reaction would be

$$MgCl_2 + 2NH_4OH \rightleftarrows Mg(OH)_2 + 2NH_4Cl.$$

And in every case, even when an excess of NH_4Cl is present, we must have the following relations at equilibrium:

$$c_{NH_4^{\cdot}} \times c_{OH'} = k_1 c_{NH_3},$$
$$c_{Mg^{\cdot\cdot}} \times c^2_{OH'} = s_{Mg(OH)_2},$$

or, by combination,

$$c_{Mg^{\cdot\cdot}} \times \left[\frac{k_1 c_{NH_3}}{c_{NH_4^{\cdot}}}\right]^2 = s_{Mg(OH)_2},$$

i.e., $$c_{Mg^{\cdot\cdot}} \times \left[\frac{c_{NH_3}}{c_{NH_4^{\cdot}}}\right]^2 = \frac{s_{Mg(OH)_2}}{k_1^2} = k, \text{ a constant.}$$

Lovén found the following concentrations at equilibrium, starting with different salts of magnesium and various concentration of ammonia and ammonium chloride, the temperature being 16–17°.

Mg	NH_3	NH_4	k
0.0203	0.0421	0.01022	0.34
0.0281	0.02027	0.0059	0 33
0.03762	0.0189	0.00655	0.31
0.1084	0.0499	0.0286	0.33

Although in the calculation of the constant *k* the ionic concentrations of Mg and NH_4 should be used in the above, complete ionization of the Mg and NH_4 salts are assumed, and the total amounts employed. As will be seen, since these concentrations were determined by ordinary analytical methods, the value of *k* is constant within the experimental limits. Lovén's own formula was expressed somewhat differently, but this form is used here so that it may be in accord with other work of the same kind.

Herz and Muhs (Zeit. f. anorg. Chem., 38, 138, 1904) studied this same equilibrium, when attained from the other direction, i.e., according to the reaction

$$Mg(OH)_2 + 2NH_4Cl \rightleftarrows MgCl_2 + 2NH_4OH.$$

Here, just as above, we have

$$c_{NH_4^{\cdot}} \times c_{OH'} = k_1 c_{NH_3}$$

and

$$c_{Mg^{\cdot\cdot}} \times c^2_{OH'} = s_{Mg(OH)_2};$$

but, since no NH_4OH was added, we know that

$$c_{NH_3} = 2c_{Mg^{\cdot\cdot}},$$

hence

$$c_{Mg^{\cdot\cdot}} \left[\frac{k_1 2c_{Mg^{\cdot\cdot}}}{c_{NH_4^{\cdot}}}\right]^2 = s_{Mg(OH)_2},$$

or

$$\frac{c^3_{\mathrm{Mg}^{\cdot\cdot}}}{c^2_{\mathrm{NH}_4^{\cdot}}} = \frac{s_{\mathrm{Mg(OH)}_2}}{4k_1{}^2} = \text{constant},$$

i.e.,

$$\frac{c^{1.5}_{\mathrm{Mg}^{\cdot\cdot}}}{c_{\mathrm{NH}_4^{\cdot}}} = \text{constant}.$$

At 29° Herz and Muhs found the following results:

Mg	**NH_4**	**Constant**
0.049	0.0771	0.141
0.0638	0.106	0.152
0.089	0.172	0.154
0.108	0.25	0.140
0.156	0.388	0.159

for ammonium chloride, while for ammonium nitrate he found

0.0495	0.076	0.145
0.0833	0.049	0.131

Here, also, the ionization is assumed to be complete, and it certainly is within a few per cent of being so. The values of the constants are not to be compared here, for unfortunately the temperatures differ widely, which would probably exercise a great influence on the ammonium hydrate solution, as well as upon the solubility, and consequently solubility product, of $Mg(OH)_2$.

In addition to these independent proofs that no complex is formed in such solutions we also have another based upon entirely different principles (Treadwell, Zeit. f. anorg. Chem., 37, 327, 1903). The molecular weight of a solution containing the chlorides of magnesium and ammonium in the ratio to form a complex

, if it did exist, can be found from the following data: .1466 gram of $MgCl_2$, and 0.1647 gram of NH_4Cl ., 1 mole of $MgCl_2$ to 2 of NH_4Cl) dissolved in 20 ms of water cause a depression of the freezing-point al to 0.°9609. From this the average molecular ght of the substance in solution is found to be 29.97. ssuming the salts to be present as a mixture, and that y are practically completely ionized (for the justification which see below), the average molecular weight would $\frac{202.32}{7}=28.9$, for a mixture of 1 mole of $MgCl_2$ and oles of NH_4Cl would dissociate into seven moles of ions. compound were formed there could not be more than e ions formed at most, and the minimum molecular ght in solution would be $\frac{202.32}{3}=67.44$.

olutions formed by each salt alone in this dilution the following results:

.1466 gram of $MgCl_2$ in 20 grams of water depresses freezing-point 0.°3956, from which $M=34.27$, instead $\frac{MgCl_2}{3}=\frac{95.26}{3}=31.75$.

nd 0.1647 gram of NH_4Cl in 20 grams of H_2O gives reezing-point depression of 0°.5511, i.e., $M=27.75$, ead of $\frac{NH_4Cl}{2}=\frac{53.52}{2}=26.74$.

hese results show that the ionization of each alone at this dilution is nearly complete, and certainly the simultaneous solution cannot change the ionization enough to significantly change the result for the average molecular weight. If the two formed a compound, the value for the average molecular weight could not under any circumstances be as low as 29.97, as we find it. This example illustrates very well the difference between a complex (or compound) salt and a simple mixture of two or more salts. In the former case the ionization is changed, i.e., a complex ion is formed; in the latter the ions formed are the same as those which exist when the substances are present alone in the solution.

The behavior of a mixture of $MnCl_2$ and NH_4Cl can be seen from the following results: 0.0968 gram $MnCl_2$ and 0.0824 gram NH_4Cl (i.e., 1 mole to 2) in 20 grams of H_2O give a depression of the freezing-point equal to $0^\circ.4797$, i.e., $M=34.56$. Assuming that the compound $[MnCl_4][NH_4]_2$ is ionized into three ions, it could not be more, the average molecular weight, just as above, would be $\frac{232.96}{3}=79.99$, while a mixture of the two, the ionization remaining unchanged, would lead to $\frac{232.9}{7}=$ 33.28.

We can conclude, then, that in such solutions, neither system forms a complex salt, and that the behavior of magnesium salts with ammonium hydrate simply depends *upon the concentration of the OH′ ion present, and upon those ions which can alter the concentration of this.*

One of the questions which gave much trouble before the inception of the electrolytic theory of dissociation was that in regard to the sequence of separation, when it is possible for two salts of differing solubility to be formed in a solution. According to the older theory it was assumed that the more insoluble one always formed first, and could be separated from the other by fractional precipitation. This, however, is found not to be in accord with the experimental facts, which, on the other hand, are perfectly represented by the law of mass action. This subject has been investigated by Findlay (Zeit. f. Phys. Chem., 34, 409, 1900) in the case of the reversible eaction

$$\underset{\text{solid}}{PbSO_4} + \underset{\text{dissolved}}{2NaI} \rightleftarrows \underset{\text{solid}}{PbI_2} + \underset{\text{dissolved}}{Na_2SO_4}.$$

Applying the law of mass action to this, since at any one temperature the concentrations of the solids in solution are constant, we have

$$\frac{c^2_{I'}}{c_{SO_4''}} = \text{constant},$$

for the reaction may also be written

$$\underset{\text{solid}}{PbSO_4} + 2I' \quad \underset{\text{solid}}{PbI_2} + SO_4''.$$

By aid of analysis, and conductivity and electromotive force observations, Findlay found the ratio $\frac{c^2_{I'}}{c_{SO_4''}}$ to be a constant for all such systems, and to have a value at 25° lying between 0.25 and 0.3. The outcome of the investigation may be summed up as follows: *From a mixed solution of sodium iodide and sodium sulphate, by the addition of a soluble lead salt, pure lead iodide (the more soluble) can be precipitated if the ratio of the square of the concentration of the iodine ion to the concentration of the sulphate ion is greater than the equilibrium constant. When the ratio becomes equal to this constant, both lead iodide and sulphate are precipitated together, the ratio* $\frac{c^2_{I'}}{c_{SO_4''}}$ *remaining constant. And all this is true for the sulphate when the ratio is smaller than the constant.*

It will be observed from these examples that by aid of the law of mass action, even though it fails to hold for strong electrolytes, we can forsee and regulate many, if not most, of the reactions with which we come in contact. Many other examples could be cited here to illustrate the methods of application, but the few above will suffice to bring out the general principles, and enable the reader to follow work of this sort. Interesting cases of ionic equilibria have also been studied by von Ende (Dissertation Göttingen, 1899), Morse (Zeit. f. phys. Chem., 41, 709, 1902), Sherrill (Zeit. f. phys. Chem., 43, 705, 1903), Sherrill and Skowronski (J. Am. Chem. Soc., 27, 30, 1905), Noyes and Whitcomb (J.

sly disappears, due
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in the water of crystallization. In this latter case, of course, the solid would exhibit the same color as the colored ion. The only correct way to find the color of the undissociated portion in solution is to use a solvent in which the substance is not dissociated to any extent; then the color can be directly observed. This is not difficult to carry out, for all solvents have a different dissociating power, and either alcohol, ether, benzene, chloroform, or acetone will be found to serve the purpose.

The ions of most acids are colorless; consequently all salts of a metal in very dilute solutions will have the same color, i.e., the color of the metallic ion. In more concentrated solutions this is not true, for many un-ionized substances are colored and, as they are now present to a greater amount, the color of the solution is the result of the mixture of these and the ions. An example of this is given by solutions of cuprous chloride, where the color of the un-ionized portion is yellow. But the copper ion is blue, hence the color of a solution of cuprous chloride may be either yellow, green, or blue, according as it is undissociated or ionized to a lesser or greater degree. All copper solutions when very dilute, provided the negative ion is colorless, show the same blue color.

The formation of a complex ion can be followed very closely when it is composed of a colored and a colorless ion. Thus if a KCN solution is added to a colored

per solution the color instantaneously disappears, due
he formation of the ion $CuCN_4''$. The formation of a
plex ion can be proven in this way, but its nature can
be shown by migration experiments, as was men-
ed above. (See Chapter IX.)

CHAPTER IX.

ELECTROCHEMISTRY.

A. THE MIGRATION OF THE IONS.

79. Electrical units.—The unit of the resistance offered to the electric current is the *ohm*, i.e., the resistance at a temperature of 0° C. of a column of mercury 106.3 cms. long, with a cross-section equal to 1 sq. mm. This is equal to 10^9 absolute units.

The unit of current strength is that strength which will separate 0.001118 gram of silver from a solution in one second, and is called the *ampere*—equal to 10^{-1} absolute units.

The unit of electromotive force is the *volt*, or 10^8 absolute units, which gives a value for the Daniell cell equal to 1.10 volts.

The unit of the amount of electricity is the *coulomb*, i.e., amperes per second; 1 gram of $H^{\cdot}$ ion carries with it 96,537 coulombs. This number is called the *Faraday*, and is designated by F.

The intensity factor of electrical energy is the volt, while the capacity factor is the coulomb, i.e.,

$$E=\epsilon\pi,$$

where ϵ is the amount of current in coulombs, π is the electromotive force in volts, and E is the electrical work the unit of which is the watt-second, equal to the volt-ampere-second, i.e., equal to 10^7 absolute units. 1 watt-second is the electrical work done when 1 ampere flows at the potential 1 volt for 1 second.

The heat equivalent of electrical energy, since the latter is equal to 1 volt×1 coulomb or 10^7 absolute units, is

$$\frac{10^7}{42600\times 980.1}=0.2394 \text{ cal.},$$

i.e., 1 watt-second $=0.2394$ cal.

To separate 1 gram of $H^{\cdot}$ ion, or the equivalent weight in grams of any other element we need then the amount of work

$$\begin{aligned}\pi\times 96540\times \text{watt-seconds} &= 96540\times 0.2394\times\pi\\ &= 23110\pi \text{ cals.},\end{aligned}$$

where π is the electromotive force of the current giving 96,540 amperes per second.

If all electrical energy is transformed into heat, then

$$\pi\epsilon=kA,$$

where A is the amount of heat and k is the heat equivalent of electrical work.

80. Faraday's law.—This is the basis of all our work in electrochemistry. The law may be expressed as follows:

1. *The amount of any substance deposited by the current is proportional to the quantity of electrictiy flowing through the electrolyte.*

2. *The amounts of different substances deposited by the same quantity of electricity are proportional to their chemical equivalent weights.*

One gram equivalent of $H^{\cdot}$ ion carries with it 96,540 coulombs of electricity, as has been determined by experiment. One coulomb, then, will cause 0.041036 gram of hydrogen ion to separate; hence it will cause the separation of $0.041036 \times a$ grams of any other element, where a is the equivalent weight of the element.

81. The migration of the ions.—The chemical effect of the passage of an electric current through an electrolyte can be divided into two distinct portions, viz., the *conduction* through the electrolyte, and the *separation* of substance at the electrodes. It is not necessary that the ions which serve for the conduction of the current through the liquid be those which are also separated at the electrode, for *secondary reactions* may take place there, causing others to appear as the result of the electrolysis. It is to be remembered, however, that even in such a case Faraday's law still holds, and the substances separated are chemically equivalent in amount to those which would have been separated in case the secondary action had been avoided.

Although the two different effects are observed together in practice, we shall consider them separately; taking up the question of conduction here, and putting off that of separation to a later period.

The conduction through the liquid depends upon what we have designated thus far as ionized matter, and varies according to the *mobility* of this, which, in turn, is dependent upon the specific nature of the matter, its concentration, the temperature, and the nature of the solvent.

After the electrolysis of a solution, *excluding, or allowing for, any secondary reaction*, it is found experimentally that the concentrations around the anode and cathode are not always identical, as they were initially. In some few cases they are, it is true, but in these it can be shown (as will be done later) that the mobility, i.e., velocity through the liquid at a certain voltage, is the same for both the anion, which goes to the anode, as it is for the cathion, which goes to the cathode. In all other cases the mobility, or speed of migration through the liquid, is different for the two kinds of ionized matter of which the substance is composed.

And further than this, the analysis of the anode and cathode liquids after electrolysis, excluding secondary reactions, leads to an expression for the relative mobilities, i.e., the migration ratio of the two ions. Indeed, wl the original solution is colored, this difference in c centration can be observed qualitatively by the eye. 1 reasons for this change, together with the princi upon which its quantitative calculation is based, w be made clear by the following considerations:

Assume the vessel in Fig. 15 to be divided into thr portions, *AC*, *CD*, and *DB*, and filled with a solutic

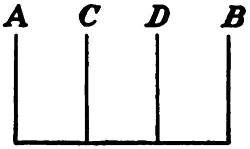

FIG. 13.

containing 30 gram equivalents of HCl. We have, tl 10 gram equivalents in each division. If 96,540 lombs of electricity are passed through the cell *A* to *B*, 1 gram equivalent of H˙ ion and 1 gram (alent of Cl′ ion will be separated upon the elec *B* and *A*, if secondary action is excluded. gases we assume to be removed as they are These 96,540 coulombs passing, as they do, thro whole solution have a certain effect upon the eq of the ions. First we will imagine the H˙ and to move with the same velocity and then with velocities, and find the relation between the concentration and the relative mobilities.

It is to be remembered here that two oppositely electrified bodies composing a system will transport a current equal to the sum of the charges carried by the two bodies in the opposite direction, for a negative charge going in one direction is equivalent to an equal and opposite charge going in the contrary direction. In other words, *all* of the current may be transported by the positive material, or a portion may be carried by each in opposite directions, and in all cases the total current is the *sum* of those currents going in the opposite directions.

I. If the velocity for each ion is the same, then 1/2 gram equivalent of Cl' ion, charged with 48,270 coulombs, will migrate from *BD* through *DC* to *CA*; and 1/2 gram equivalent of $H^{\cdot}$ ion, with the same amount of electricity, will go from *AC* through *CD* to *DB*. Altogether, then, 1 gram equivalent, charged with 96,540 coulombs, has passed through the section *CD*. Since 1 gram equivalent of $H^{\cdot}$ ion has been removed by decomposition from *BD* and 1/2 gram equivalent has migrated to it, we have left 9½ gram equivalents of $H^{\cdot}$ ion and 9½ gram equivalents of Cl' ion, since but 1/2 gram equivalent of this has migrated from it. Consequently we have in *BD* 9½ gram equivalents of HCl. In *AC* we have the same number, since 1 gram equivalent of Cl' ion has disappeared and 1/2 gram equivalent has migrated to it and 1/2 gram equivalent of $H^{\cdot}$ ion has migrated from it. In the section *DC* the concentration is unaltered, i.e., just as much ionized matter has left it as has been carried to it.

The concentration at the anode is the same as that at the cathode, then, after the electrolysis of a solution composed of ions with the same mobility.

II. *Assume* the velocity of the $H^{\cdot}$ ion to be five times that of Cl'.

In this case, after 1 gram equivalent of H and 1 gram equivalent of Cl have separated in the gaseous state, the whole system will have suffered a change. 5/6 of a gram equivalent of $H^{\cdot}$ ion, charged with $\frac{5}{6}$(96,540) coulombs, will migrate from *AC* through *DC* to *BD*, and 1/6 of a gram equivalent of Cl' ion, with $\frac{1}{6}$(96,540) coulombs, will go from *BD* through *CD* to *AC*. Altogether, as before, 1 gram equivalent of ion will go through the section *CD*, carrying with it 96,540 coulombs of electricity.

The original composition of the solution in *CD* is again unchanged. In *BD* we have lost 1 gram equivalent of $H^{\cdot}$ ion in the form of gas, and gained 5/6 of a gram equivalent by the migration; consequently we have $9\frac{5}{6}$ gram equivalents of $H^{\cdot}$ ion left. 1/6 of a gram equivalent of Cl' ion has migrated from it, so that in *BD* we have $9\frac{5}{6}$ gram equivalents of HCl.

In *AC* we have lost 5/6 of a gram equivalent of $H^{\cdot}$ ion and 1 gram equivalent of Cl' ion as gas, but have ined 1/6 of a gram equivalent of Cl′ by the migran; consequently we have $9\frac{1}{6}$ gram equivalents of Cl left.

From these two examples the following law may be duced: *The loss on the cathode (BD) is related to it on the anode (AC) as the mobility of the anion (Cl′) to that of the cathion (H˙).*

In this way Hittorf determined the relative mobilities migration ratios of the various ions.

82. Determination of the migration ratios.—The praccal determination of the relative mobilities is merely matter of analysis. The apparatus which is used r this purpose is a decomposition-cell, so arranged at no metal can drop from one electrode to the other; r a U tube may serve the purpose, so long as the two ortions of liquid may be removed and analyzed sepaately. The apparatus is filled with solution and the urrent passed through for a certain length of time, the lectrodes being of the metal which is contained in the alt or inert, except in cases where certain secondary ctions are to be avoided. After a certain time either he anode or cathode portion is withdrawn and analyzed. This analysis will give us the loss of metal on the one lectrode, from which that on the other may be calulated.

If *n* is the fraction of the cathion which has migrated rom the anode to the cathode when one gram equivalent has been separated, then $1-n$ is that fraction of the anion which has gone to the anode. These two quantities, n and $1-n$, are called the migration ratios of the cathion and anion. We have then

$$\frac{n}{1-n}=\frac{\text{loss at anode}}{\text{loss at cathode}}=\frac{U_c}{U_a},$$

where U_c is the mobility of the cathion and U_a that of the anion.

An example will make the determination of this clear: Hittorf electrolyzed a solution of $AgNO_3$ until 1.2591 grams of Ag were separated. The volume of liquid at the cathode before the experiment gave 17.46249 grams of AgCl, and after it but 16.6796 grams, i.e., a loss of 0.7828 gram of AgCl or of 0.5893 gram of Ag.

If no Ag had come to the cathode by migration, the solution would have lost 1.2591 grams of Ag; it lost, however, only 0.5893 gram; hence $1.2591-0.5893=0.6698$ gram Ag has come to it by the migration. If just as much of the Ag had come by migration as had been separated, the migration ratio of the Ag would have been 1, i.e., the NO_3' ion would not have migrated. Only 0.6698 gram of Ag has migrated, however; hence the migration ratio for the $Ag^{\cdot}$ ion in $AgNO_3$ can be found by the proportion

$$1.2591:0.6698::1:x=0.532;$$

the migration ratio of the NO_3' ion is

$$1 - 0.532 = 0.468.$$

These values are not the same for all dilutions, although in general the variation is but slight.

A table containing a large number of results from experiments of this sort is given by Kohlrausch and Holborn, Leitvermögen der Elektrolyte, a few of which will be found in Table XIV.

TABLE XIV.

HITTORF'S MIGRATION RATIOS FOR THE IONS.

Solutions 1/10 equivalent normal.

Substance.	$1-n$	Substance.	$1-n$
1/2 K_2SO_4	0.60	NH_4Cl	0.508
1/2 $CuSO_4$	0.64	1/2 $BaCl_2$	0.61
1/2 H_2SO_4	0.21	1/2 $CaCl_2$	0.68
/2 K_2CO_3	0.37	1/2 $MgCl_2$	0.68
/2 Na_2CO_3	0.48	HCl	0.21
/2 Li_2CO_3	0.59	KNO_3	0.50
OH	0.74	$NaNO_3$	0.61
aOH	0.84	$AgNO_3$	0.526
Cl	0.507	1/2 $Ca(NO_3)_2$	0.61
aCl	0.63	$KClO_3$	0.46
Cl	0.70		

Naturally, inert anodes can also be used for this pur- se, and in many cases, to avoid secondary reactions, anode which is different from the metal of the salt ay be used. Thus Hittorf (Ostwald's Klassiker der akten Wissenschaften, Nos. 21 and 23) used cad- ium as an anode in determining the migration ratio of sodium chloride, to avoid the H˙ ion due to the reaction of chlorine on water.

When the substances separated at the electrodes are known, analysis of the liquids at the cathode and anode enable us to find the nature and composition of the ions into which the substance dissociates. In most cases here qualitative observations suffice for the purpose, and often color-changes make it possible to follow the process, even without analysis. Examples of this method are to be found in many investigations, see, for example, Noyes and Blanchard (J. Am. Chem. Soc., 22, 729 and 732, 1900), Peters (Zeit. f. phys. Chem., 26, 229, 1898), Calvert (ibid., 38, 535, 1901), Morse (ibid., 41, 709, 1902), and McBain (Z. f. Elektrochem., 11, 961). The use of agar-agar or gelatine in these cases enables us to obtain the solution in the form of a jelly, its conduction relation remaining almost unchanged (see p. 207).

B. THE CONDUCTIVITY OF ELECTROLYTES.

83. The specific conductivity. — In measuring the electrical conductivity of a solution we obtain results in two different units: one refers to the same amount of all solutions, the *specific conductivity;* the other refers to the equivalent or molecular amount, the *molecular, or equivalent, conductivity.*

The unit of conductivity is the conductivity which a column of a length of 1 *cm. and a cross-section of* 1 *cm.*^{2}

sses when its resistance is one ohm. The best coning aqueous solutions of strong acids have this conivity at about 40°. The conductivities based on unit are designated by κ.

. Molecular and equivalent conductivity.—Since the luctivity of a solution depends almost exclusively the amount of substance dissolved in it, it is more venient for us to express our results in molecular quivalent terms.

he equivalent (molecular) conductivity of a substance e conductivity of the solution which contains 1 *equiva-* (1 *mole*) *of substance, the electrodes being separated cm. and large enough to contain between them the e solution.* This value can be found by dividing κ the number of equivalents (moles) per cubic centir, or by multiplying κ by the number of cubic centirs in which 1 equivalent (1 mole) is dissolved. n V is the volume containing 1 equivalent (or 1) in liters, then

$$\kappa \times 1000 \times V_e = \Lambda$$

$$\kappa \times 1000 \times V_m = \mu,$$

e equivalent conductivity is designated by Λ and cular conductivity by μ.

85. Determination of electrical conductivity.—Since the degree of dissociation of electrolytes can be determined most accurately by aid of the conductivity, the method is one of great importance. The apparatus used for this purpose was designed by Kohlrausch,* and is similar to that for determining the resistance of metals, except that an alternating current is used in place of the direct, and a telephone receiver instead of the galvanometer. The alternating current is used here to prevent actual decomposition of the solution, for that would decrease its concentration continually and cause polarization of the electrodes. In this way all substance which is deposited by the current in one direction is redissolved by it in the opposite direction, and all polarization effect is nullified.

The form of the electrode is shown in Fig. 16, the connections being made by aid of the mercury in the glass tubes. The electrodes themselves are of Pt, which are coated electrolytically with platinum-black, so as to do away with any difference of potential between them.

It is not necessary to have these electrodes just a square centimeter in cross-section or 1 cm. apart, for we can easily find the factor which will transform results for any cell into terms of specific conductivity. Kohlrausch has carefully determined the specific conductivity of a number of standard solutions, so that a determination of any one of these in a larger or smaller cell will give directly the factor necessary to transform results by that cell into actual specific conductivities, according to the definition. For a 0.02 molar solution of KCl, Kohlrausch found the values $\kappa_{18^\circ}=0.002\,397$, $\Lambda_{18^\circ}=119.85$, $\kappa_{25^\circ}=0.002\,768$ and $\Lambda_{25^\circ}=138.54$.

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* For details see Ostwald, Handbook of Physicochemical Measurements, Macmillan & Co.

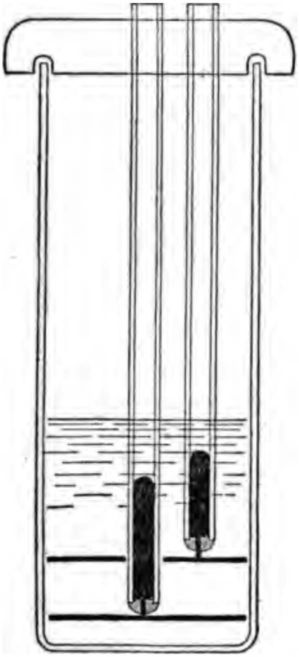

FIG. 14. (Natural size.)

86. Ionic conductivities.—Since the ions are the carriers of electricity in solution, the equivalent conductivity at any dilution divided by that at infinite dilution, i.e., when the substance is present only in the form of ions, will give us the degree of dissociation. We have then

$$\alpha=\frac{\Lambda_v}{\Lambda_\infty}.$$

This conductivity at infinite dilution means simply that the equivalent conductivity is not altered by further dilution. This maximum value for the equivalent conductivity Kohlrausch found for a binary electrolyte *to be equal to the sum of two single values, one of which refers to the anion and the other to the cathion. This law of the independent migration of the ions* shows that conductivity is an *additive property.* The truth of this law is shown in Table XV.

TABLE XV.

MOLECULAR CONDUCTIVITIES AT INFINITE DILUTION.

	K	Na	Li	NH_4	H	Ag
Cl	123	103	95	122	353	...
NO_3	118	98	..	...	350	109
OH	228	201	..	...	...	...
ClO_3	115	...	..	...	...	103
$C_2H_3O_2$	94	73	..	...	...	83

ra

differences of two corresponding sets of numbers

tical rows, and of any two in the horizontal ones,

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* Fo

ments, M

are nearly equal, which can only occur when the result is composed of two single and independent values.

One kind of ion, then, always carries the same amount of electricity with its own velocity, independent of the nature of its companion ion.

The equivalent conductivity at infinite dilution is consequently

$$\Lambda_\infty = l_c + l_a$$

where l_c and l_a are the equivalent conductivities of the ions of the substance in solution at infinite dilution.

We have then (p. 394)

$$n = \frac{l_c}{l_c + l_a} = \frac{l_c}{\Lambda_\infty} \quad \text{and} \quad 1 - n = \frac{l_a}{\Lambda_\infty},$$

in other words, $l_c = n\Lambda_\infty$, $l_a = (1-n)\Lambda_\infty$.

Thus the molecular conductivity at infinite dilution μ_∞ (equal here to the equivalent conductivity Λ_∞) of sodium chloride is 110, while $n = 0.38$ and $1 - n = 0.62$, hence

$$l_c = 0.38 \times 110 = 41.8(\mathrm{Na}^{\cdot}),$$

$$l_a = 0.62 \times 110 = 68.2\,(\mathrm{Cl}'),$$

i.e., 1 *mole of* $Na^{\cdot}$ *ion possesses a conductivity of* 41.8 when between electrodes 1 cm. apart *and large enough to* *contain between them the total volume of solution in which the sodium ion exists; and* 1 *mole of* Cl' *ion under the same conditions has a conductivity equal to* 68.2.

In all solutions in the same solvent, at the same temperature, these values remain constant, so that it is possible for us to calculate what the conductivity would be for any substance at infinite dilution. This is of great use in experimental work, for it is not always possible to actually reach this limiting value with any degree of accuracy.

A table of such results, then, enables us to find the limiting value of the conductivity at infinite dilution, and not only this, for

$$\Lambda_v = \alpha(l_a + l_c),$$

i.e., *if we know the fraction of a mole of each ion present we can find the equivalent conductivity of the solution at any dilution by multiplying the sum of the ionic conductivities by the degree of ionization.*

Since most neutral salts are very largely ionized the value of the equivalent conductivity can be readily determined. By subtracting the value for the metal ion from this result it is possible, then, to find the ionic conductivity of the acid radical which is present as the negative ion. In the table below are given a few ionic conductivities, from which various values may be calculated.

IONIC CONDUCTIVITIES AT 18° AND INFINITE DILUTION.*

	l	Temp. Coeff.		l	Temp. Coeff.
....	33.44	0.0265	$\frac{1}{2}\,\mathrm{Zn}^{\cdot\cdot}$......	45.6	0.0251
....	43.55	0.0244	$\frac{1}{2}\,\mathrm{Mg}^{\cdot\cdot}$....	46.0	0.0256
....	64.67	0.0217	$\frac{1}{2}\,\mathrm{Ba}^{\cdot\cdot}$......	56.3	0.0238
....	67.6	0.0214	$\frac{1}{2}\,\mathrm{Pb}^{\cdot\cdot}$......	61.5	0.0243
....	68.2	0.0212	$\frac{1}{2}\,\mathrm{SO}_4''$.....	68.7	0.0227
....	64.4	0.0222	$\frac{1}{2}\,\mathrm{CO}_3''$.....	70	0.0270
....	66	0.0215	BrO_3'......	46.2	......
....	54.02	0.0229	ClO_4'......	64.7	......
....	46.64	0.0238	IO_4'.......	47.7	......
....	65.44	0.0216	MnO_4'.....	53.4	......
....	67.63	0.0215	CHO_2'.....	46.7	......
....	66.40	0.0213	$\mathrm{C_2H_3O_2}'$....	35	......
....	56.63	0.0211	$\mathrm{C_3H_5O}'$.....	31	......
....	55.03	0.0215	$\mathrm{C_4H_7O_2}'$....	27.6	......
....	33.87	0.0234	$\mathrm{C_5H_9O_2}'$....	25.7	......
....	61.78	0.0205	$\mathrm{C_6H_{11}O_2}$....	24.3	......
....	318	......	$\frac{1}{2}\mathrm{C_2O_4}$.......	62.7	......
....	174	......	Picrate ion...	26	0.0258

'he temperature coefficients here are the percentage nge in ionic conductivity per centigrade degree.

'he ionic conductivity of elementary ions is a periodic ction of the atomic weight and rises with it in each es of analogous elements; but analogous elements with nic weights greater than 35 have approximately equal luctivities.

omeric and metameric anions have the same equiva- conductivities.

7. The conductivity of organic acids.—The deter- ation of the ionization constant of organic acid, ch has been discussed above, is very easily accom- hed by aid of the conductivity. By substituting for α in the Ostwald dilution law we obtain

$$\frac{\mu_v^2}{\mu_\infty(\mu_\infty-\mu_v)}=KV.$$

See Kohlraush, Berl. Akademieber. 26, 581, 1902, and Sitzungsber. kad. d. Wiss *zu Berlin, 26,* 572, 1902; Bredig, Z. f. phys. Chem., *91, 1894; and Gorke, ibid., 61,* 495, 1908.

For inorganic acids, bases, and salts, for which the Ostwald dilution law does not hold, we can use either the Rudolphi or the van't Hoff dilution law, which become, by substitution of $\frac{\mu_v}{\mu_\infty}$ for α,

$$\frac{\left(\frac{\Lambda_v}{\Lambda_\infty}\right)^2}{\left(1-\frac{\Lambda_v}{\Lambda_\infty}\right)\sqrt{V}}=\text{const.}$$

and

$$\frac{\left(\frac{\Lambda_v}{\Lambda_\infty}\right)^3}{\left(1-\frac{\Lambda_v}{\Lambda_\infty}\right)^2 V}=\text{const.}$$

The molecular conductivity, when the acid is very weak and dilute, is found from the experimentally determined value of κ, after subtracting from it the value κ_{H_2O} for the water used, for these two terms, under these conditions, become of the same order.

88. **Determination of hydrolytic dissociation from the conductivity.**—When a salt reacts with 1 mole of water and either base or acid or both, are appreciably ionized, the larger the hydrolytic dissociation, the greater will be the equivalent conductivity, up to $\Lambda_A+\Lambda_B$ as a limit.

The increase of conductivity for the dissociation α will be $\Lambda_2 - \Lambda_1$, when Λ_2 is the actual equivalent conductivity of the water solution of the salt, and Λ_1 is the equivalent conductivity without hydrolytic dissociation at the same concentration. (This is found from the conductivity of the salt in the presence of an excess of one of the products, subtracting from it the conductivity of the added substance, if it has any). $\Lambda_A + \Lambda_B - \Lambda_1$ is the increase of conductivity, then, that would be observed if the hydrolysis were complete. Hence

$$\alpha = \frac{\Lambda_2 - \Lambda_1}{\Lambda_A + \Lambda_B - \Lambda_1},$$

where $\Lambda_A + \Lambda_B$ is the sum of the conductivities of the acid and base at the same dilution as the salt.

An example of the calculations in this way is the following:

At 25°, $V = 197.6$. Λ for aniline hydrochloride is 126.7; Λ for aniline hydrochloride plus an excess of aniline is 106.6; Λ_{HCl} is 415 ($V = 197.6$). The conductivity of aniline is negligible. Find the degree of hydrolytic dissociation.

Here $126.7 - 106.6$ is the actual increase in conductivity due to the hydrolytic dissociation α. If the hydrolysis were complete this increase would be $415 - 106.6$;

It is conceivable here that instead of an increase in conductivity due to the hydrolysis that a decrease might occur, i.e., where the acid at the dilution of the salt had a smaller conductivity than the salt. Then it would be necessary simply to change the ratio so as to give the actual decrease to the decrease caused by $\alpha = 1$.

For the method to be used in case both acid and base are very slightly ionized, see Lundén, J. chim. Phys., 5, 145 and 574, 1907, and Noyes, Carnegie Publication No. 63.

89. The absolute mobility of the ions.—Thus far we have considered only the relative mobility of the ions, or else their conductivities; now, however, we shall consider the actual velocity in centimeters per second with which they go through the solution.

Imagine two electrodes 1 cm. apart, and assume between them a solution containing 1 equivalent mole of positive and 1 equivalent mole of negative ions. In one second the amount of electricity Λ_∞ will go over. Each equivalent mole of ions would transport 96,540 coulombs of electricity; hence the ratio $\frac{\Lambda_\infty}{96540}$ will give the fraction of the distance, 1 cm., which the ions together have traversed in one second, i.e., the sum of their velocities in centimeter-seconds. In other words, we have the distances $\frac{l_a}{96540}$ and $\frac{l_c}{96504}$ traversed by each kind of ion, for since $\Lambda_\infty = l_a + l_c$, $\frac{\Lambda_\infty}{96540} = \frac{l_a}{96540} + \frac{l_c}{96540}$.

The molecular conductivity of a 0.0001 normal solution of KCl at 18° (in reciprocal ohms) is 128.9; the sum of the distances traversed by the two ions, then, is

$$\frac{128.9}{96540}=0.001345 \text{ cm. per second.}$$

This total velocity is made up of the two single velocities. By Hittorf's experiments the relative velocities of $K^{\cdot}$ and Cl' ions in KCl are in the ratio of 49 to 51. Hence $K^{\cdot}$ has a velocity of 0.00066 cm. per second and Cl' has a velocity of 0.00069 cm. per second in a 0.0001 molar solution at 18°, for a potential difference of 1 volt.

Knowing the absolute mobility of the ions we can also thus calculate the equivalent conductivity at infinite or any other dilution. We have, in the two cases,

$$\frac{\Lambda_\infty}{96540}=U_a+U_c$$

and
$$\frac{\Lambda_v}{96540}=\alpha(U_a+U_c),$$

where U_a and U_c $\left(\text{equal to } \frac{l_a}{96540} \text{ and } \frac{l_c}{96540}\right)$ are for infinite dilution, and expressed in centimeters per second at a definite temperature. In the table below are some of the absolute mobilities as given by Kohlrausch.

ABSOLUTE VELOCITY OF THE IONS AT 18° IN CMS. PER SECOND.

$K^{\cdot} = 0.00066$
$NH_4^{\cdot} = 0.00066$
$Na^{\cdot} = 0.00045$
$Li^{\cdot} = 0.00036$
$Ag^{\cdot} = 0.00057$
$Cr_2O_7'' = 0.000473$
$H^{\cdot} = 0.00320$
$Cl' = 0.00069$
$NO_3' = 0.00064$
$ClO_3' = 0.00057$
$OH' = 0.00181$
$Cu^{\cdot\cdot} = 0.00031$

It has been possible to prove the correctness of some of these results by experiment, i.e., by actual speed measurements on a color boundary in a tube. Whetham's method for this purpose (Phil. Trans., 1893A, 337; 1895A, 507) is as follows: If we consider the boundary-line of two equally dense solutions which contain a common colorless ion, but which are colored differently, and call the salts *AC* and *BC*, then when a current passes through the boundary-line the *C* ion go in one direction and the *A* and *B* ions in the other. If the *A* and *B* ions are the cathions, then the color boundary will move in the direction of the current, and its velocity will be equal to the velocity of the ion which causes the change of color. In this way the velocities for $Cu^{\cdot\cdot}$, Cr_2O_7'', and Cl' were determined in centimeter-seconds. In the table on p. 409 the values found in this way are compared with those calculated by Kohlrausch.

For other methods for determining the mobilities of the ions see Masson (Phil. Trans., 192A, 331, 1899);

Steele (Phil. Trans., 198, 105, 1902); Abegg and Gans (Zeit. f. phys. Chem., 40, 737, 1902), and Denison (Zeit. f. phys. Chem., 44, 575, 1903).

COMPARISON OF ABSOLUTE IONIC VELOCITIES.

Ion.	Whetham, by Experiment.	Kohlrausch, Calculated.
$Cu^{\cdot\cdot}$	0.00026	0.00031
	0.000309	
Cl'	0.00057	0.00069
	0.00059	
	0.00047	
Cr_2O_7''	0.00048	0.000473
	0.00046	

90. The basicity of an acid.—For all binary organic acids the formula

$$K=\frac{(\mu_v)^2}{\mu_\infty(\mu_\infty-\mu_v)V}$$

holds strictly. For dibasic acids this is also true when the dissociation is not more than 50%, i.e., all dibasic organic acids under these conditions ionize as monobasic acids. In the case of the neutral salts of these acids, however, the dissociation into more than two ions takes place at a much smaller dilution. The difference of conductivity, then, between two dilutions must be greater for the neutral salt of a polybasic acid than for one of a monobasic one. Ostwald has made use of this fact for the determination of the basicity. He found empirically that the *Na salt* of a monobasic acid gives a difference in equivalent conductivity at $V=32$ $V=1024$ liters of approximately 10 units, a of 20 units, etc. Hence to find the basicity we have only to find the equivalent conduct Na salt at 32 and 1024 liters dilution; then n, of the acid, is given by $n=\frac{\Delta}{10}$.

VALUES OF Δ AND n FOR SODIUM SALTS OF ORGAN

Acid.	Δ
Formic	10.3
Acetic	9.5
Propionic	10.2
Benzoic	8.3
Quininic	19.8
Pyridin-tricarboxylic (1, 2, 3)	31.0
" (1, 2, 4)	29.4
Pyridin-tetracarboxylic	41.8
Pyridin-pentacarboxylic	50.1

91. The conductivity of neutral salts.—A pirical law enables us to find the equivalent c of a neutral salt at one dilution, provided for another, and the salt is largely ionized Λ_v is not very different from Λ_∞. The relatio is as follows:

$$\Lambda_\infty-\Lambda_v=n_1\cdot n_2\cdot c_v,$$

or

$$\Lambda_\infty=n_1\cdot n_2\cdot c_v+\Lambda_v,$$

where n_1 and n_2 are the valences of the anion and cathion respectively, and c_v is a constant for all electrolytes. When c_v is known for all dilutions, and also the terms Λ_v, n_1, and n_2, we can find the value of Λ_∞, i.e., the equivalent conductivity at infinite dilution. If we designate $(n_1 \cdot n_2 \cdot c_v)$ by d_v, then

$$\Lambda_\infty = \Lambda_v + d_v.$$

Table XVI gives the value of d_v for different dilutions and for values of $n_1 \cdot n_2$ equal to 1, 2, and 4 at both 18° and 25°.

TABLE XVI.

V	Equiv. per liter.	Both ions univalent.		1 ion uni- and the other bi-valent.		Both ions bi-valent.	
		18°	25°	18°	25°	18°	25°
10000	0.0001	1.0	1.1	2.0	2.3	5	6
5000	0.0002	1.4	1.6	2.8	3.2	7	8
2000	0.0005	2.0	2.3	4.4	5.1	11	13
1000	0.001	2.7	3.1	6.1	7.0	16	18
500	0.002	3.6	4.2	8.3	9.6	23	26
200	0.005	5.5	6.3	12.3	14.2	33	38
100	0.01	7.5	8.6	16.5	19.0	42	48
50	0.02	9.8	11.3	21.5	24.5	51	58

This behavior may be summed up in words as follows: *The decrease of equivalent conductivity is roughly constant for salts of the same type; and the decrease in equivalent conductivity for salts of different types is proportional to the valences of the ions.*

This is similar to the relations already considered between the ionization of salts of the same type (pp. 195–197); in fact, they were derived from this.

92. The ionization of water.—The ions of water are

$H^{\cdot}$ and OH', i.e., to a very slight degree it is a binary electrolyte. The specific conductivity κ of a specially purified water was found by Kohlrausch to be

$0.014 \cdot 10^{-6}$ at 0° C.
$0.040 \cdot 10^{-6}$ at 18°
$0.055 \cdot 10^{-6}$ at 25°
$0.084 \cdot 10^{-6}$ at 34°
$0.17 \cdot 10^{-6}$ at 50°

One mm. of this water at 0° has a resistance equal to that of a copper wire of the same section and 40,000,000 kilometers long, i.e., which is long enough to go around the earth a thousand times.

From this conductivity the degree of dissociation is easily determined. One mole of $H^{\cdot}$ ion has a conductivity equal to 318 units (p. 381), while 1 mole of OH' ion has one equal to 174; hence the maximum molecular conductivity of water should be $\Lambda_{\infty}=318+174=492$, if completely dissociated. That of a liter between electrodes 1 cm. apart at 18° is 10^3 times as large as 0.04×10^{-6}, i.e.,

$$0.04\times10^{-6}\times10^{3}=0.04\times10^{-3},$$

hence

$$\frac{0.04\times10^{-3}}{492}=0.8\times10^{-7};$$

which is the concentration of $H^{\cdot}$ and OH' ions in moles per liter at 18°, or there are 17 grams of OH' and 1 gram of $H^{\cdot}$ ion in 12,000,000 liters of water.

It is to be remembered here that the 492 would be the value if 1 mole of $H^{\cdot}$ ion and 1 mole of OH' ion were present together between electrodes 1 cm. apart and of any cross-section, so long as they will contain between them the amount of solution. Since we use water as a solvent, the equivalent conductivity is usually calculated for a liter, and not, as it might be assumed by definition, 18 grams. The calculation was similar in determining the ionic product of $H^{\cdot}$ and OH' ions (p. 339), where s_{H_2O} was equal to $\frac{1000}{18}K$, i.e., $55.5K$.

93. The temperature coefficient of conductivity.—According to Kohlrausch, the conductivity varies with the temperature as follows:

$$\mu_t = \mu_{18}[1 + \beta(t - 18)];$$

where β is the temperature coefficient, or the change in conductivity for 1° C. We can find β by experiment from the equation

$$\beta = \frac{\mu_t - \mu_{18}}{\mu_{18}(t - 18)}.$$

Substances with small molecular conductivities usually have large temperature coefficients. Most of the strongly dissociated salts have a value for β equal to 0.025, i.e., the equivalent conductivity changes $2\frac{1}{2}\%$ for each degree.

This temperature coefficient depends upon several factors, for the internal friction of the solvent changes, as well as the degree of dissociation and the velocity of migration. It is only possible to obtain a negative coefficient when the dissociation decreases enough to more than compensate for the increase in the velocity due to the diminished friction; consequently all such substances must have negative heats of dissociation.

The equivalent conductivity at infinite dilution also increases with the temperature, so it must not be imagined that the ionization increases in this way. The examples already given (p. 325) will serve to show how α varies with the temperature.

94. The conductivity of difficultly soluble salts.—If the saturated solution of any insoluble salt is so dilute that we may assume complete dissociation, $\varLambda_\infty = \varLambda_v$, we have

$$\kappa_{\text{solution}} - \kappa_{H_2O} = \kappa.$$

and
$$\varLambda_v = \varLambda_\infty = \kappa \times 1000V,$$

i.e.
$$V = \frac{\varLambda_\infty}{\kappa \times 10^3}$$

and
$$C = \frac{1}{V} = \frac{\kappa \times 10^3}{\varLambda_\infty} \text{ moles per liter.}$$

This method has been used by Holleman * and Kohlrausch and Rose † with very good results. In this way a number of solubilities have been determined; although it is usually customary for more accurate work, to first find the approximate dilution in this way and then by aid of the table on page 411 to find from it and Λ_v a more accurate value to be used in place of Λ_∞, the final value of $V = \frac{1}{c}$ being calculated from that. Thus

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* Zeit. f. phys. Chem., 12, 125, 1803. † Ibid., 234, 1893.

1 part $BaSO_4$ dissolves in 429,700 parts H_2O at 16°.1 C.,
1 part $SrSO_4$ dissolves in 10,070 parts H_2O at 24°.2 C.,
1 part $BaCO_3$ dissolves in 45,566 parts H_2O at 24°.3 C.,
1 part $SrCO_3$ dissolves in 91,468 parts H_2O at 24°.3 C.

$BaSO_4$ is of course so insoluble that it is impossible to find its term Λ_∞ by experiment. Its value, however, can be found from the general equation

$$\Lambda_\infty(MX) = \Lambda_\infty(MX_1) + \Lambda_\infty(M_1X) - \Lambda_\infty(M_1X_1),$$

where M and M_1 represent metals and X and X_1 the negative radicals.

Thus from

$$\left.\begin{array}{ll} \Lambda_\infty, \text{ for } \tfrac{1}{2}\,BaCl_2, & = 115 \\ \Lambda_\infty, \text{ for } KCl, & = 122 \\ \Lambda_\infty, \text{ for } \tfrac{1}{2}\,K_2SO_4, & = 128 \end{array}\right\} 18^\circ$$

we have

$$\Lambda_\infty, \text{ for } \tfrac{1}{2}BaSO_4, = 115 + 128 - 122 = 121.$$

This value could also be found from the table illustrating Kohlrausch's law of the independent migration of the ions, of which it is an application, or from that on p. 403. Naturally, solubilities calculated from this value of Λ_∞ would be expressed in liters containing 1 equivalent, while solubilities are usually expressed in moles per liter. The V directly found for $\frac{1}{2}BaSO_4$ then must be multiplied by two to give the volume containing 1 mole; and the solubility in moles per liter would be $c=\frac{1}{2V}$. It must be borne in mind here that this method is only applicable, in its simpler form, when we can safely assume Λ_v for a saturated solution to be the same as Λ_∞. And further, it is limited to those substances which are soluble enough to give a value of κ which differs appreciably from that for the water used. Silver iodide solutions in this respect seems to be about on or just beyond this limit.

95. The dielectric constant and dissociating power. Other solvents than water.—According to J. J. Thomsen and Nernst, there is a relation between the dielectric constant of the solvent and its power of dissociating dissolved substances. The dielectric constant is determined by placing the substance between two plates between which there is a certain potential difference, and measuring the loss of potential. Air is used first between the plates, and then the substance to be determined. The factor which we measure is the specific inductive capacity of the liquid for electricity, referred to air as a standard. The dielectric constants of a number of solvents are given in the following table.

Benzene	2.24
Ether	4.25
Amyl alcohol	16.05
Ethyl alcohol, 99.8%	25.8
Water	79.6

As will be observed, the constant for water is higher than for any of the other solvents, and its dissociating power is also the greatest.

The latest theory as to the relation between the dielectric constant and dissociating power is by Brühl.* The dielectric, i.e., the solvent, acts just as the glass in a Leyden jar and prevents the ions from neutralizing their charges. The greater the dielectric constant, then, the greater the amount of free ions which may exist in the solution. This connection between the dielectric constant and dissociation, as found by electrical and other means, may be considered as very strongly confirmatory of the theory of dissociation into charged components or ions.

The electrical behavior of substances in many non-aqueous solvents is very different from that in water, and it is difficult from our present knowledge to see how they can be governed by the same laws. For examples in some cases the equivalent conductivity does not attain a maximum constant value, but after attaining a maximum decreases with further dilution; and the degree of ionization determined electrically does not in all cases agree with that determined by the boiling-point, for instance. Further than this, the conductivity cannot in all cases be said to be the sum of two independent values, i.e., of those of the ions.

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* Zeit. f. phys. Chem., 30, 1, 1899.

We cannot but infer, then, from our present knowledge that the process of solution is quite different for these than for water. Neither the Ostwald nor any other form of a dilution law seems to hold in these cases. In other words, the electrical behavior of these is inexplicable as yet, and until the processes taking place in such systems is better understood little of our data can be generalized. There is one exception to all this, however. Franklin and Kraus (Am. Chem. J., 23, 277, 1900) have found that dilute binary electrolytes in liquefied ammonia-gas give an approximately constant value for the Ostwald dilution law, at least a value which very much more nearly constant than that obtained in a water solution. For concentrated solutions in the same solvent, see Franklin and Kraus (J. Am. Chem. Soc., 27, 191, 1905).

The behavior of metallic sodium in liquefied ammonia (Cady, J. Phys. Chem., 1, 707, 1897, and Franklin and Kraus, l. c., p. 306) is very peculiar, for the conduction is apparently more metallic than electrolytic. No products of decomposition are observed and there is no polarization, while the conductivity is exceedingly high.

Among the tables at the end of this book will be found one giving the conductivities of substances in various non-aqueous solvents, from which an idea, at any rate, may be obtained as to their relations toward the electric current.

96. The conductivity of mixtures of substances having an ion in common.—The conductivity of a solution containing two substances with an ion in common can be readily shown to be given by the formula

$$\kappa=\frac{1}{p(v_1+v_2)}(\alpha_1 v_1 n_1 \Lambda_{\infty 1}+\alpha_2 v_2 n_2 \Lambda_{\infty 2}),$$

where v_1 and v_2 are the volumes of the two simple solutions which are mixed, i.e., v_1+v_2 is the total volume of solution containing n_1+n_2 equivalents of the two substances. α_1 and α_2 are the degrees of ionization of the substances *in the mixture*, $\Lambda_{\infty 1}$ and $\Lambda_{\infty 2}$ are the equivalent conductivities of the two substances in a simple solution, and p is the ratio of the volume of the mixture to the sum of the constituent volumes.

For the freezing-point of such a mixture, in an analogous way, we have

$$\Delta=[M_1N_1(1+\alpha_1(m_1-1))+M_2N_2(1+\alpha_2(m_2-1))],$$

where m is the number of moles of ions produced from one original mole, M_1 and M_2 are the molecular depressions (p. 175) in 1 liter of the simple solutions and N_1 and N_2 are the number of moles per liter of each.

For substances for which the Ostwald dilution law holds there is, naturally, no difficulty in determining the terms α_1 and α_2 (p. 306); and for strong electrolytes it is also possible, although the process is not always so simple.

For illustrations of the use of these formulas and the calculation of the values α_1 and α_2 the reader must be referred elsewhere,* for it would lead us too far to consider them in detail here. It will be observed, however, that it is assumed in the above formula that $\Lambda_{\infty 1}$ and $\Lambda_{\infty 2}$ are not altered by the mixing, a supposition which probably holds only for solutions weaker than 0.5 normal.

Noyes and Kohr (J. Am. Chem. Soc., 24, 1145–1146, 1902) give an example of the calculation of the degree of ionization of such substances when mixed, which is based upon another principle and somewhat simpler than the other methods. The principle upon which this determination is based is as follows: The dissociation of a substance in the presence of another with an ion in common is that which the conductivity measurements show it to have when it is alone present at a concentration of its ions equal to the square-root of the product of the concentration of its ions in the solution of the mixed salts. This principle was demonstrated by solubility experiments (Noyes and Abbott, Zeit. f. phys. Chem., 16, 138, 1895).

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* See MacGregor (Trans. Nova Scotia Inst. of Science, 9, 101, 1896); Barnes (ibid., 10, 124, 1900); Archibald (ibid., 9, 291, 1898; also Trans. R. S. of Can. (2), 3, 89, 1897); and Schrader (Z. f. Elektrochem., 3, 498, 1897).

It was found there *that for those substances which do not follow the Ostwald dilution law the concentration of the un-ionized part of a salt has the same value, when the product of the concentrations of its ions has the same value, whatever may be the two separate factors of that product.* In a mixture of potassium chloride and potassium hydroxide, for example, where the former is 0.0033 molar and the latter 0.35, we first assume the ionization to be 85% for each (as an approximation). The product $c_{K^{\cdot}} \times c_{Cl'}$ then has the approximate value, $(0.35+0.0033) \times 0.85 \times 0.0033 \times 0.85$. The square root of this quantity (or 0.030) is then 85% of the concentration (0.0355) of pure potassium chloride at which the degree of dissociation is the same as it is in the solution of the mixed potassium salts. The degree of dissociation is then to be ascertained from a plot of the molar conductivity values. For potassium chloride in this way we find α to be 0.90; and by the same procedure α for the KOH is found to be 84%.

In mixtures of substances without an ion in common, the same general formula for the conductivity and freezing-point (p. 419) is also to be employed. Here, however, there may be a reaction between the substances which would give rise to a new substance. In such a case, this, also, must be considered, and treated just as the others. All these things also hold for mixtures of more than two substances, although in such cases the calculation is considerably more complicated (see MacGregor, Trans. Roy. Soc. Can. (2), 2, 65, 1896).

C. ELECTROMOTIVE FORCE.

97. Determination of the electromotive force.—In all the cases we are to consider in this section it is necessary that the electromotive force be measured by aid of the compensation method, i.e., that as little actual current be taken from the cell as is possible.

As the basis of such methods is a known and constant electromotive force, the standard cell is an exceedingly important part of the measurement. The standard cells in general use in this work are of two kinds, one of which has a fixed constant value, while the other may be made up in such a way as to give one of several values.

The former one is the Clark cell, Fig. 15, which consists of amalgamated Zn in a paste of $ZnSO_4$ and Hg in a paste of Hg_2SO_4. This cell gives an E.M.F. equal to

$$1.4328-0.00119(t-15)-0.000007(t-15)^2.$$

Another standard cell in common use is the cadmium element (Weston). This is made up with electrodes

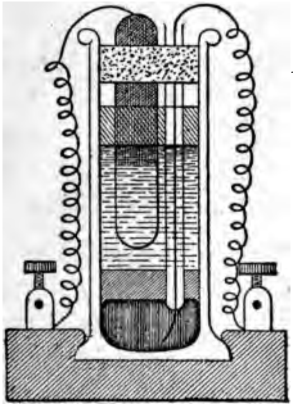

FIG. 15.

of mercury and cadmium amalgam according to the following scheme, the Hg being the positive pole:

$$Hg-\underbrace{Hg_2SO_4+CdSO_4}_{\text{paste}}$$

$$\text{sat. } CdSO_4+\text{crystals}$$

$$\underbrace{CdSO_4}_{\text{paste}}-\text{Cd amalgam.}$$

The electromotive force of this cell is

$$1.0186+0.00004(20-t) \text{ volts.}$$

The Helmholtz element, Fig. 16, consists of amalgamated Zn in $ZnCl_2$ solution (sp. gr. = 1.409 at 15°), calomel, and Hg. This gives an E.M.F. approximately equal to 1 volt, but its exact value depends upon the sp. gr. of the $ZnCl_2$ solution so that it must always be measured by comparison with a Weston or Clark element. Its great advantage is its very small temperature coefficient, which at low temperatures is negligible.*

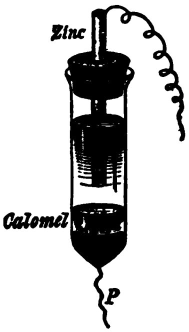

FIG. 16.

98. Types of cells.—Cells are either reversible or non-reversible, according as the process may be reversed or not. A reversible cell can always be put in its original condition again by sending a current through it in the opposite direction, while with a non-reversible cell this is not possible. A typical reversible cell is the Daniell, where we have Cu in $CuSO_4$ and Zn in $ZnSO_4$.

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* For further details of these measurements, cells, etc., see Ostwald's Physico-chemical Measurements, Macmillan.

The Zn dissolves and Cu is precipitated during the action, but by passing a current through it from Cu to Zn the Zn is precipitated, while Cu is dissolved, until the original state is again reached.

A non-reversible cell, on the other hand, is any one from which a gas is given off, for the passage of the current cannot cause the gas to recombine. Here we shall consider principally the reversible type.

99. The chemical or thermodynamical theory of the cell.—The simplest theory of the action of a reversible cell was advanced by Helmholtz and Thomson. According to this, the chemical energy of the process is transformed completely into electrical energy. This theory in the form in which it was advanced, however, has proven to be incorrect, for it holds only for the Daniell cell. The explanation of the variation in the case of other cells was offered by Gibbs and Helmholtz independently, who proved it to be due to the temperature.

Assume a reversible primary cell in which the amount of heat q is liberated or absorbed when one equivalent of the ions has been carried from one side to the other. Imagine this cell in a temperature-bath so that the cell remains at constant temperature,—i.e., if heat is absorbed it is replaced, or if heat is liberated it is removed —thus preventing q from causing a change in temperature.

It is quite evident, if the chemical energy of a reaction is being transformed completely into electrical energy, and no heat is either evolved or absorbed as the reaction progresses, that the chemical energy (expressed as heat) transformed is equivalent to the electrical energy produced, i.e.,

$$E_c = E_e.$$

If the reaction evolves or asborbs heat, however, it will be necessary, if the temperature is to be kept constant, to remove or supply heat to the system, and it is clear that this will involve either a decrease or increase in the electrical energy produced. In short, in addition to E_c, we must know the effect of this absorbed or liberated heat upon the electrical energy, if the total amount produced by the cell is thus to be calculated. This can be calculated by the following ideal cyclic process: Heat the cell from the temperature T to $T + \Delta T$. The electromotive force will then go from π to $\pi + \Delta\pi$. The cell is now allowed to run until the amount of current ε_0 has been developed. In order that the cell may be retained at this constant temperature the heat $q + \Delta q$ must be absorbed, and the electrical work done by the cell will be $\varepsilon_0(\pi + \Delta\pi)$.

Next cool the cell again to T, where the electromotive force is π and send the amount of current ε_0 through it in the opposite direction, thus doing the electrical work $\varepsilon_0\pi$. Heat equal to q must be removed to keep the temperature constant at this point, and, provided the cell is reversible, all will again attain its original condition.

The total work involved in the cycle of operations is $\varepsilon_0(\pi+\Delta\pi)-\varepsilon_0\pi$, i.e., $\varepsilon_0\Delta\pi$, and the amount of heat Δq has been transformed into work, hence by the 2d law of thermodynamics (p. 58) we have

$$\frac{\Delta q}{q}=\frac{\varepsilon_0\Delta\pi}{q}=\frac{\Delta T}{T},$$

i.e.,

$$q=\varepsilon_0 T\frac{\Delta\pi}{\Delta T},$$

and the correct relation between the chemical and electrical energies becomes

$$E_e=\pi\varepsilon_0=E_c+\varepsilon_0 T\frac{\Delta\pi}{\Delta T},$$

or

$$\pi=\frac{E_c}{\varepsilon_0}+T\frac{\Delta\pi}{\Delta T}.$$

The electrical energy producable from chemical energy is equal to the heat of the chemical reaction, expressed in electrical units, plus the temperature times the temperature coefficient of the electrical energy, which may be either positive or negative.

The actual E.M.F., π, is only equal to that calculated from the chemical energy when $\frac{\Delta\pi}{\Delta T}=0$, i.e., for the [illegible] the E.M.F. does not change with the temperature. Otherwise π is smaller or greater than $\frac{E_c}{\epsilon_0}$ according as $T\frac{d\pi}{dT}$ is negative or positive.

The Daniell cell has such a small temperature coefficient that the electrical energy is nearly equal to the chemical energy. For other cells it is possible to determine the temperature coefficient, and thus from the chemical energy to calculate the E.M.F. of the cell. The results by experiment and calculation agree in most cases within the experimental error, showing that this conception of the process is correct. We see, then, that the amount of heat generated by the chemical process is no criterion of the amount of electrical energy involved, for heat which is absorbed from the environment may also be transformed into electrical energy, and in other cases less heat may be transformed into electricity than is given up by the chemical process.

An example of the application of this formula is given by the Grove gas cell. Here

$$\pi=1.062 \quad \text{and} \quad E_c=34200,$$

hence

$$1.062=\frac{34200}{23110}+T\frac{d\pi}{dT}, \quad \text{i.e.,} \quad T\frac{d\pi}{dT}=-0.418V,$$

place of -0.416, as found by experiment. The value 10 here is obtained from $96540 \times 0.2394 \times \pi = 23110\pi$ s., and is the work in calories necessary for the osition of 1 gram equivalent of any substance at olts.

oo. The osmotic theory of a cell.—Considering a l from the standpoint of our conclusions respecting nature of electrolytes in solution, it is possible to more clearly into the cause of the rise of a difference potential between two solutions or a metal and a ution.

ssume that we have two solutions in contact, and t they contain the same *monovalent* ions in different centrations. The difference of potential existing on ir boundary can be calculated by aid of the following cess of reasoning: If U_a and U_c are the mobilities of respective ions, then, by the passage of 96,540 coubs of electricity, the following changes take place: the current enters on the concentrated side and passes ough both solutions, $\frac{U_c}{U_c+U_a}$ gram equivalents (moles) positive ion will go from the concentrated to the dilute ution, and during the same time $\frac{U_a}{U_c+U_a}$ gram equivats (moles) of negative ion will go from the dilute to the ncentrated side. Let p be the osmotic pressure of the sitive and negative ions in the concentrated solution, and p' that of those in the dilute solution. The maximum work to be done by the process, then, will be (p. 407),

$$\frac{U_c}{U_a+U_c}RT\log_e\frac{p}{p'}-\frac{U_a}{U_a+U_c}RT\log_e\frac{p}{p'}$$

$$=\frac{U_c-U_a}{U_a+U_c}RT\log_e\frac{p}{p'},$$

and this must be equal to $\varepsilon_0\pi$ for the process going in this way, i.e., to the electrical work done at the surface of contact of the two solutions. Since R is in calories this value will also be expressed in calories. To transform it into electrical units it is only necessary to divide through by 23,110. This relation was derived and tested experimentally by Nernst (Zeit. f. phys. Chem., 4, 129; 1888), who found it to hold true within the experimental error.

If U_c is greater than U_a we could expect, then, that a weaker solution of an acid or base, when superimposed on a stronger one, would show the polarity of the faster moving ion. In other words in diffusing through the solution the faster ion would impart its polarity to the weaker solution. With acids, indeed, we do observe that the dilute solution is positive, while with bases it is negative; and this is in accord with our previous observations that $H^{\cdot}$ and OH' are the ions possessing the greatest mobility or velocity. This process does not result in a complete separation of the ions nor even in more than ery slight one, for it must be remembered that the kinds of electricity attract one another, the conse- nce of which is that the speed of the faster moving s is decreased, while that of the slower is increased.

his same method of reasoning will also enable us understand the action of the arrangement

centrated amal- m of the metal M.	Water solution of a salt of the metal M.	Dilute amalgam of the metal M.

this case the passage of 96,540 coulombs will cause ram equivalent of the metal M to go from the con- trated side to the dilute, and, if there are n_v equiva- ts to the mole, the maximum work per equivalent be

$$\frac{1}{n_v} RT \log_e \frac{c_1}{c_2},$$

re c_1 and c_2 are the concentrations of the metal M he amalgams. Again, here, if this expression is so sformed as to give electrical units instead of calories, division by 23,110 (i.e., 96,540×0.2394), it will the value of π the electromotive force of the cell rating in this way.

nd the same is true for cells with electrodes of the e soluble metal and two concentrations of a solution a salt or salts of that metal. Consider, for example, cell

$$\mathrm{Cu}\left|\begin{array}{c}\text{dilute}\\ \mathrm{CuSO_4}\end{array}\right.\overset{\longrightarrow}{\left|\begin{array}{c}\text{concentrated}\\ \mathrm{CuSO_4}\end{array}\right|}\mathrm{Cu.}$$

By passing a current through this cell in the direction of the arrow the following changes will take place:

1. For each 96,540 coulombs of electricity 1 gram equivalent of copper will dissolve from the electrode in the dilute solution, i.e., will be transformed from the metallic to the ionic state.

2. At the boundary of the two solutions the process described above will take place; and

3. One gram equivalent of $Cu^{\cdot\cdot}$ ion will be deposited from the concentrated solution upon the electrode.

As the result of processes (1) and (3) 1 gram equivalent of $Cu^{\cdot\cdot}$ ion will go from the concentrated to the dilute solution. The maximum work of this process, then, for each 96,540 coulombs will be

$$\frac{RT}{n_v}\log_e\frac{p_1}{p_2},$$

where n is the valence of the metal and p_1 and p_2 are the osmotic pressures of the $Cu^{\cdot\cdot}$ ion in the two solutions.

By the second process (contrast with direction of current in the case above) we have as the work

$$\frac{RT}{n_v}\cdot\frac{U_a-U_c}{U_a+U_c}\log_e\frac{p_1}{p_2}.$$

This second value is usually so small, when compared to the other, that it may generally be neglected, and the two differences of potential between the electrodes and the solutions measured separately.

Neglecting the difference of potential between the liquids, then, we have

$$\pi=\frac{RT}{n_v\varepsilon_0}\log_e\frac{p_1}{p_2},$$

or, including the potential difference between the solutions,

$$\pi=\frac{RT}{n_v\varepsilon_0}\cdot\frac{2U_a}{U_a+U_c}\log_e\cdot\frac{p_1}{p_2},$$

i.e., the sum of the two, where R must be given in electrical units, if π is to be expressed in volts.

By separating the amount of work $\frac{RT}{n_v}\log_e\frac{p_1}{p_2}$ into two portions, so that each will give the maximum work at an electrode, we can write

$$\frac{RT}{n_v\varepsilon_0}\log_e\frac{P}{p_2}-\frac{RT}{n_v\varepsilon_0}\log_e\frac{P}{p_1},$$

where P is a constant for any one metal at the same temperature, in the same solvent, and is called the *electrolytic solution pressure.* The portions containing the expressions $\log_e\frac{P}{p}$ will then give the difference of potential of copper in dilute copper sulphate and copper in concentrated copper sulphate.

The *electrolytic solution pressure* assumed to exist in this way is analogous to the ordinary solution pressure which we have already considered, except in this case it is for the solution of a metal or any other element, i.e., is the pressure with which element tends to attain the ionic state.

When we consider a stick of metal in a solution of one of its salts, we have, if P is the electrolytic solution pressure and p is the osmotic pressure of the metal ion in the solution, three possibilities:

1. $P = p$.
2. $P > p$.
3. $P < p$.

The behavior in these three cases we shall consider.

1. $P = p$. We shall observe no action, since the two opposing pressures are equal and consequently cancel.

2. $P > p$. This is the case with Zn. $Zn^{\cdot\cdot}$ ion will go from the electrode into the solution, taking with it positive electricity. This will take place only to a very slight degree, for it would increase the positive charge of the solution. This positive matter around the electrode will then be attracted back to the plate, which is negatively charged owing to the loss of positive ion. We have then, finally, the metal negative against the solu-

n, and the electrode surrounded by what is known as Helmholtz double layer, in this case a layer of positive n on a negative plate. If positive electricity is given w to the metal, the double layer is broken up and re Zn will go into solution in the ionic form, but as n as the current is stopped the double layer will again formed.

3. $P<p$. This is true for Cu. A stick of copper a solution of one of its salts will have $Cu^{\cdot\cdot}$ ion from solution deposited upon it, since the pressure toward Cu is greater than that away from it. This $Cu^{\cdot\cdot}$ es positive electricity with it, consequently the metal positive against its solution. The double layer will o be formed here, for the positive charge on the metal l attract negative ion from the solution. In this case, wever, the double layer will be broken up when elecity is conducted away from the Cu, so that the $Cu^{\cdot\cdot}$ n will again precipitate and continue to do so until $= P$, when all action will cease. Since 1 gram equivat of any ion carries with it 96,540 coulombs of elecity, the amount of metal going in or out of solution y be infinitesimal and still cause the production of a asurable amount of electricity.

The relations of Cu and Zn in their respective solutions are shown in Fig. 17.

The double layer is formed on both. Until the Cu d Zn are connected by a wire the equilibrium as it is will be undisturbed. When they are connected current will go through the wire from Cu to Zn, i Zn$^{\cdot\cdot}$ ion will go into the solution, depositing an equiv lent amount of Cu$^{\cdot\cdot}$ ion upon the copper plate. T electromotive force will then depend on the differen between the two values of P, if p is the same on bot

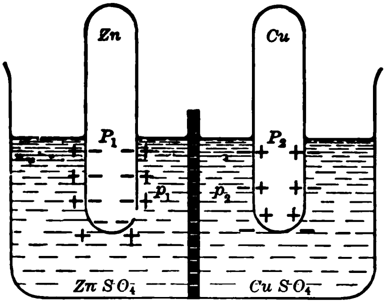

FIG. 17.

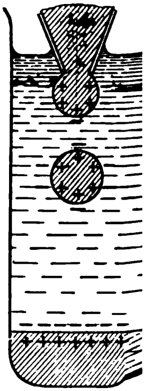

FIG. 18.

sides, and the amount of current will depend upon t number of gram equivalents of Zn dissolved and of C precipitated.

The value of the osmotic counter-pressure, it will seen, regulates the behavior of the metal, i.e., indicat whether it will dissolve or not. Thus Cu and Ag di solve when KCN is added to their solutions; this mean that the osmotic pressure of the ions of Ag$^{\cdot}$ or Cu$^{\cdot\cdot}$ i the solution is smaller than the solution pressure, for th

$Cu^{\cdot\cdot}$ or $Ag^{\cdot}$ ions combine with CN' to form a complex ion and are thus removed from the system.

The presence of a layer of ion around the charged metal has been proven by Palmaer (Wied. Ann., 18, 257, 1899) by an arrangement shown in Fig. 18.

Drops of mercury are allowed to fall into a weak solution containing mercurous ion, metallic mercury being in the bottom of the tube containing the solution. If now the double layer theory is true, the drops of Hg as they form should have the electricity of the $Hg_2^{\cdot\cdot}$ ion deposited upon them, and these positively charged drops should then attract negative ion, forming on each a double layer. When such a drop reaches the mercury at the bottom it will unite with that, forming once more ions of $Hg_2^{\cdot\cdot}$ and releasing those of the negative radical, and the concentration of mercury salt will be greater at the bottom than at the top. Palmaer's experiments showed this difference in concentration to actually exist.

Experiment has shown that the metals Na, K . . . , etc., up to Zn, Cd, Co, Ni, and Fe are always negative against their solutions, i.e., $P > p$.

The noble metals, on the contrary, are positive against their solutions, although in some few cases it is possible to get a solution in which $P > p$. In general, though, for the noble metals $P < p$.

A negative element has exactly the same action except that, in general, as far as is known, $P > p$. Here, although

$P > p$, the electrode is positive against the solution, for the negative ion formed from the electrode leaves positive electricity behind.

In general, the electrolytic solution pressure depends upon the temperature, the nature of the solvent, and the concentration of the substance in the electrode (see p. 422).

101. Mathematical expression of the osmotic theory of the cell.—It is possible from the above conception of solution pressure to derive the formula giving the value of the E.M.F. of a single electrode of any metal in a solution of one of its salts. This will depend upon the osmotic pressure of the metal ions working in the one direction and upon the electrolytic solution tension working in the other. Since the ion goes from one pressure to the other, a certain amount of work is done and this amount must always be the same no matter in what form it appears, i.e., whether electrical or osmotic.

When 1 mole of ion is transferred from the pressure P to the pressure p, the osmotic work done is equal to

$$\int_p^P RT\frac{dp}{p} = RT\int_p^P \frac{dp}{p},$$

from which, by integration, we obtain

$$RT \log_e \frac{P}{p}.$$

The corresponding electrical work, however, is $\pi\varepsilon_0$, where π is the difference of potential between the metal and solution and ε_0 is the amount of electricity carried by 1 gram equivalent of ions. We have then

$$\pi\varepsilon_0 = RT \log_e \frac{P}{p},$$

or

$$\pi = \frac{RT}{\varepsilon_0} \log_e \frac{P}{p},$$

from which we see that if $P = p$, $\pi = 0$.

ε_0 for 1 mole of a monovalent ion (i.e., for 1 equivalent) is equal to 96,540 coulombs. We must, however, express both sides of the equation in electrical units. Since $R = 2$ cals., the right side of the equation must be divided by 0.2394 in order to obtain our result in electrical units. We have then

$$96{,}540 \times \pi(\text{volts}) = \frac{2}{0.4343 \times 0.2394} T \log \frac{P}{p},$$

or

$$\pi = 0.0575 \log \frac{P}{p} \text{ volts at } 17^\circ \text{ C.}$$

For a divalent element we must multiply ε_0 by 2; hence if n_v is the valence of the metal, we have

$$\pi = \frac{0.0002}{n_v} T \log \frac{P}{p} \text{ volts,}$$

or for negative ions

$$\pi = -\frac{0.0002}{n_v} T \log \frac{P}{p} = \frac{0.0002}{n_v} T \log \frac{p}{P} \text{ volts.}$$

If we consider a cell composed of two metals, each present in a solution of one of its salts, the difference of potential may arise (1) at the place of contact of the two metals, (2) at the place of contact of the two solutions, and (3) and (4) at the points of contact of the two electrodes with their solutions. The first can be entirely neglected provided the temperature remains constant. The second, as was mentioned above, is always small, so that we shall have to consider here only (3) and (4), assuming, when necessary, that the value has been determined as on page 441. At 17° the E.M.F. of the cell will be, then,

$$\pi = (\pi_1 - \pi_2) = \frac{0.0575}{n_{v_1}} \log \frac{P_1}{p_1} - \frac{0.0575}{n_{v_2}} \log \frac{P_2}{p_2} \text{ volts,}$$

the minus sign being used because a ion is formed on the one side, and consequently must disappear upon the other, for there must always be an equivalent amount of positive and negative ions in the solution.

102. The measurement of the potential difference between a metal and a solution.—The method in use for the determination of differences of potential is based upon the use of a normal electrode, i.e., an electrode in a solution of one of its salts, of which the potential difference is known. Making up a cell by combining this electrode with the one to be measured, it is possible, from observations of the resulting electromotive force, to find the value of the unknown potential difference. The original measurement of the potential difference of the normal electrode was made by forming a cell with this and another electrode, having a potential of zero against its solution. The electromotive force of this combination, then, is identical with the potential difference to be found. Such an electrode with zero potential is formed when mercury flows into a solution of an electrolyte (KCl), for any differences of potential existing between the mercury and solution must eventually be eliminated by the continually dropping mercury.

The electrodes in general use are made up according to one of the two following schemes:

$$HgCl \text{ in molar } KCl/Hg,$$

or

$$HgCl \text{ in } 0.1 \text{ molar } KCl/Hg;$$

the former giving a difference of potential of −0.56 volt, the latter of −0.0613, both at 18°. The sign in each case here refers to the solution, i.e., the solution is negative against the metal.

Fig. 19 shows the form of the cell. The syphon tube is so arranged that it is always kept full of the KCl solution. This dips into the liquid of the other electrode, provided they form no precipitate. In case they do, a molar solution of KNO_3 is used, into which the siphons from the two electrodes dip. The advantage of using KNO_3 as a connector is that the mobilities of the $K^{\cdot}$ and $NO_3{}'$ ions are nearly the same; hence the passage of the current produces no change in the concentration at the two sides and consequently gives rise to no difference of potential.

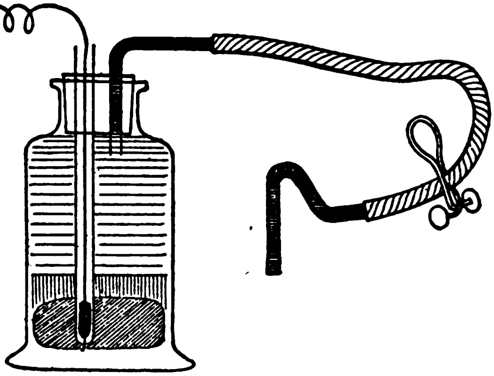

FIG. 19.

hence the copper must be more positive than the Hg by 0.585 volt.

103. The heat of ionization.—Knowing the difference of potential existing between a metal and a solution, and its rate of change with a variation in the temperature, it is possible from the formula on page 427 to find the heat of ionization of the metal. We found then that

$$E_e = E_c + \varepsilon_0 T \frac{d\pi}{dT},$$

or

$$\pi = \frac{E_c}{\varepsilon_0} + T\frac{d\pi}{dT}.$$

The term E_c, here, is the heat produced when 1 gram equivalent of the metal goes from the metallic to the ionic state, and its value is given by the formula

$$E_c = \left(\pi - T\frac{d\pi}{dT}\right)\varepsilon_0.$$

But (page 429),

$$\varepsilon_0\pi = 96540 \times 0.2394 \times \pi \text{ volts} = 23110\pi \text{ cals.};$$

hence the heat of ionization E_c, for 1 gram equivalent can be found from the relation

$$E_c = \left(\pi - T\frac{d\pi}{dT}\right) 23{,}110 \text{ cals.}$$

For copper in copper acetate (molar) at 17°, $\pi=0.6$, and $\frac{d\pi}{dT}=0.000774$, while $\frac{d\pi}{dT}$ for copper in copper sulphate is 0.000757, i.e., an average value of $\frac{d\pi}{dT}$ of 0.000766 volts, hence E_c, the heat of ionization of copper, is 8736 cals. per gram equivalent, or 17,472 cals. per mole. It was in this way that the value for H was determined for use in the table given on page 232.

104. Concentration-cells.—*a. In which the electrodes have different concentrations.*—If the electrodes are made of two amalgams of the same metal in salts of this metal the E.M.F. is given by the formula

$$\pi=\frac{0.0002}{n_v}T\log\frac{P_1}{p_1}-\frac{0.0002}{n_v}T\log\frac{P_2}{p_2}\text{ volts.}$$

If the two solutions have the same concentration of metal ions, then $p_1=p_2$, and we have

$$\pi=\frac{0.0002}{n_v}T\log\frac{P_1}{P_2}\text{ volts,}$$

when P_1 and P_2 are the electrolytic solution pressures of the two electrodes with respect to the dissolved metal.

Amalgams when dilute may be considered as solutions, in which the mercury acts as the solvent; consequently the osmotic pressure of the metal in the amalgam will proportional to the electrolytic solution pressure of electrode. Since in all solutions the osmotic pressure proportional to the concentration, we may substitute the electrolytic solution pressures the proportional ns, the concentrations of the metal in the two electrodes. We obtain then

$$\pi = \frac{0.0002}{n_v} T \log \frac{c_1}{c_2} \text{ volts.}$$

is formula was proven experimentally by G. Meyer it. f. phys. Chem., 7, 477, 1891); see also Cady (J. ys. Chem., 2, 551–564, 1898); and Richards and bes (Carnegie Publication No. 56, 1907), some of ose results for zinc amalgams in a $ZnSO_4$ solution are en in the table below.

TABLE XVII.

T	c_1	c_2	π (obs.)	π (calc.)
11°.6	0.003366	0.00011305	0.0419 v.	0.0416 v.
18°	0.003366	0.00011305	0.0433 v.	0.0425 v.
12°.4	0.002280	0.0000608	0.0474 v.	0.0445 v.
60°	0.002280	0.0000608	0.0520 v.	0.0519 v.

he results obtained by Meyer also proved the formula old copper for amalgams in $CuSO_4$, etc., solutions.

Ve have assumed the metals to dissolve in mercury as notomic molecules in this case, and the assumption upheld by our results, not only by this method but also others.

f Zn had been present in the form of diatomic molees in the mercury, our equation would have had a erent value. For the movement of the same amount of ions as before, we should have had, then, the osmotic work equal to

$$\frac{1}{2}\cdot\frac{RT}{0.4343}\log\frac{c_1}{c_2},$$

and since the electrical work would have been the same as before, i.e.,

$$2\times 96540\pi,$$

we should have had

$$\pi=\frac{1}{2}\cdot\frac{0.0002}{2}T\log\frac{c_1}{c_2}\text{ volts};$$

i.e., the E.M.F. would have been one-half what we have found it to be.

The electromotive force is found, then, to be dependent only upon the concentration of the metal in the amalgam and its valence, and not upon the nature of the metal itself. The mercury has no effect so long as the metal dissolved in it gives the larger E.M.F.

Another example of the electrodes having different electrolytic solution pressures, owing to differences of concentration, is given by cells of the type of the Grove gas-battery in an altered form. The electrodes are of platinized platinum, in which the gas is absorbed under different pressures, and are placed partly in the liquid ly in gas of corresponding (partial) pressure. electrode is to be considered as a perfectly revers- electrode,* i.e., one from which ions of the absorbed as a gas are given up, for the metal ly as a conductor, as has been shown experi- by the use of different metals, the same result ways obtained. In this way reversible gaseous s of all kinds can be made. Oxygen as an , however, gives off OH′ ion and absorbs O OH′ ion gives up its charges to it.

have two electrodes of H, under different pres- contact with a liquid containing H˙ ion, we ain a certain E.M.F. This may be calculated ways, as we did in the case of amalgams. In d way, however, the process is slightly different, mole of H gas forms two equivalents of mono- n (p. 189). The osmotic work is equal to

$$\frac{RT}{0.4343} \log \frac{P_1}{P_2},$$

. The electrical work, however, which corre- this is $2\epsilon_0\pi$, for $H_2 = 2H^{\cdot}$, hence

$$\pi = \frac{RT}{2\epsilon_0(0.4343)} \log \frac{P_1}{P_2};$$

---

ectrolytic solution pressure here of the gas electrode is l to the *n*th root of the gaseous pressure, where *n* is the num- oining weights in one formula weight of gas.

i.e., we have 2 in the denominator notwithstanding that the gas is monovalent.

b. Different ionic concentrations.—In this type of cell we assume the electrodes to be of the same metal, but dipping into solutions which possess different ionic concentrations of the metal. An example is given by the arrangement

$$\mathrm{Ag(AgNO_3\ conc.) - (AgNO_3\ dilute)Ag.}$$

From the general equation we have

$$\pi = \frac{RT}{\varepsilon_0} \log_e \frac{P_1}{p_1} - \frac{RT}{\varepsilon_0} \log_e \frac{P_2}{p_2}.$$

Or, since $P_1 = P_2$,

$$\pi = \frac{RT}{\varepsilon_0} \log_e \frac{p_1}{p_2},$$

where p_1 is the osmotic pressure of the $Ag^{\cdot}$ ion on the concentrated side and p_2 that on the dilute side.

From this we see that the E.M.F. depends only upon the ratio of the concentrations, and not at all upon the actual concentrations, all of which was found to hold experimentally by Nernst (l. c. p. 430).

Since the osmotic pressure is proportional to the ncentration, we may substitute the latter for the mer; we obtain

$$\pi=\frac{RT}{n_v\varepsilon_0}\log_e\frac{c_1}{c_2}.$$

The concentration of $Ag^{\cdot}$ ion in a 0.01 molar solution AgNO$_3$ is 8.71 times as great as that in a solution ich is 0.001 molar (not 10 times), hence the E.M.F. 18°) of a cell made up of Ag in these two concentions of AgNO$_3$ should be

$$\pi=0.0002\times291\log 8.71=0.054 \text{ volt,}$$

ile 0.055 volt was found by experiment.

Since at 17° C. we have

$$\pi=\frac{0.0575}{n_v}\log\frac{c_1}{c_2}\text{ volts,}$$

oncentration ratio of the ions equal to 10, would give =0.0575 volt for a monovalent ion, or 0.02875 volt for divalent one.

This class includes all cells made up of solutions ntaining different concentrations of metal ions. In se the contact of the two liquids causes the forman of a precipitate, another solution is used between, two being connected by small siphons.

105. Dissociation by aid of the electromotive force. nce for concentration-cells we have the formula

$$\pi=\frac{RT}{n_v\varepsilon_0\times0.4343}\log\frac{c_1}{c_2}\text{ volts,}$$

or for monovalent metals

$$\log\frac{c_1}{c_2}=\frac{\pi}{0.0002T},$$

we can find the ionic concentration of the metal on the one side provided that on the other is known.

An example of this is the cell as given by Morgan:

$$Ag-\frac{m}{10}AgNO_3-KNO_3-\frac{m}{20}KAgCN_2-Ag,$$

which gives an E.M.F. of 0.542 volt, Ag in $AgNO_3$ being the positive pole.

If, for simplicity, $AgNO_3$ 0.1 molar is considered as completely dissociated, the concentration of $Ag^{\cdot}$ ion will be 0.1 molar, and, since $T=273+17=290°$, we have

$$\log\frac{c_1}{c_2}=\frac{0.542}{0.0002\times 290}, \quad c_2=3.1\times 10^{-11};$$

i.e., in the $m/20$ $KAgCN_2$ solution the $Ag^{\cdot}$ ion is present to a concentration of 3.1×10^{-11} molar.

This method was devised by Ostwald, and is one of the most delicate known, for the more dilute the one solution is, i.e., the smaller the concentration of its metal ions, the greater is the E.M.F. of the cell, and the greater the accuracy of the result.

Another typical cell of this kind is

$$Ag - \frac{m}{10} AgNO_3 - KNO_3 - \frac{m}{10} KCl\ AgCl - Ag,$$

which was used by Goodwin to determine the solubility of AgCl.

In a saturated water solution of AgCl we may assume without error that the dissociation is complete. The solubility product will then be

$$c_{Ag^{\cdot}} \times c_{Cl'} = s.$$

Since in a pure water solution of AgCl, $Ag^{\cdot} = Cl'$, the square root of s, s being determined under any conditions at constant temperature, will give directly the concentration of $Ag^{\cdot}$ (or Cl') in the solution. And, if complete ionization may be assumed, this is equal to the solubility of AgCl under these conditions.

For example, if we find the E.M.F. of the cell

$$Ag - AgCl\ KCl - AgNO_3 - Ag,$$

where $c_{Cl'}$ on the left and $c_{Ag^{\cdot}}$ on the right are known, we can calculate $c_{Ag^{\cdot}}$ on the left, and consequently s and the solubility of AgCl.

Goodwin (Zeit. f. phys. Chem. 13, 577, 1894) found, when the concentration of $AgNO_3$ and KCl was 0.1 molar, an average E.M.F. of 0.45 volt at 25°. By conductivity measurements at 25° we find

α (for $AgNO_3 m/10$) $=82\%$ and α (for $KCl m/10$) $=85\%$, so that

$$\log\frac{c_1}{c_2}=\frac{0.450}{0.0002\times 298},$$

or

$$c_2=1.94\times 10^{-9};$$

i.e., $Ag^{\cdot}$ ion is present in a 0.1 molar KCl solution of AgCl to a concentration of 1.94×10^{-9} moles per liter. The product s is then found to be equal to

$$1.94\times 10^{-9}\times 0.085=s=1.64\times 10^{-10}$$

and

$$\sqrt{s}=1.28\times 10^{-5};$$

i.e., AgCl in a saturated water solution at 25° is present to a concentration of 1.28×10^{-5} moles per liter.

A cell of this sort may be arranged with bromides, iodides, etc., in place of the chlorides, which was also done by Goodwin, and the solubility of AgBr and AgI determined.

Another illustration of this method of determining dissociation is furnished by Ostwald's arrangement for determining the dissociation constant for water. The scheme is a gas-cell in the form

H – Acid........Base – H,

when the two H electrodes have the same solution pressure. The E.M.F. of such a cell, deducting the E.M.F. caused by the contact of the two solutions, is, for molar solutions at 17° C.,

$$\pi = 0.0575 \log \frac{c_1}{c_2}.$$

Here, contrary to the case for electrodes of different gaseous concentration, the 2 does not appear in the denominator (page 449), for that factor simply refers to the process taking place between the electrode and the gas. In this case the electrodes remain constant and the same, and only the osmotic pressures of the $H^{\cdot}$ ion is to be considered. By experiment $\pi = 0.81$ volt; hence, since $c_1 = 0.8$ (i.e., the normal acid is 80% dissociated),

$$\frac{c_1}{c_2} = 10^{14},$$

or

$$c_2 = 0.8 \times 10^{-14}.$$

Since this is the concentration (in terms molar) of the $H^{\cdot}$ ion in the base, and the concentration of the OH' ion in contact with them is 0.8, the ionic product for H_2O is

$$0.8 \times 0.8 \times 10^{-14}.$$

Since H_2O dissociates into $H^{\cdot}$ and OH' ions, the concentration of $H^{\cdot}$ and OH' ions in pure water is the same, and is equal to

$$\sqrt{(0.8)^2 \times 10^{-14}} = 0.8 \times 10^{-7} = H^{\cdot} \text{ and } OH' \text{ ions in } H_2O.$$

From the conductivity also, at this temperature, Kohlrausch found

$$0.8 \times 10^{-7}.$$

It would be possible in this case to use oxygen electrodes, by which the same final result would be obtained, but platinum black absorbs very little oxygen, so that the results are not as certain as with hydrogen.

For the measurement of the concentration of the ion of mercury the normal electrode serves as the basis. The concentration of $Hg_2^{\cdot\cdot}$ ion in the normal electrode has been found to be 3.5×10^{-18} moles per liter (Ley and Heimbucher, Zeit. f. Electrochem., 10, 303, 1904). Since $\frac{Hg_2^{\cdot\cdot}}{Hg^{\cdot\cdot}}$ 120, in the presence of metallic mercury, according to Abel (Zeit. f. anorg. Chem., 26, 377, 1901), it is possible to find the concentration of $Hg^{\cdot\cdot}$ in the normal electrode; it is equal to 2.9×10^{-20} moles per liter. By measurements of the electromotive force of a combination of mercury in a solution containing $Hg^{\cdot\cdot}$ or $Hg_2^{\cdot\cdot}$ ions, with the normal electrode we can thus determine the concentration of these ions. For further details as to this, see Sherrill and Skowrouski, J. Am. Chem. Soc., 27, 30, 1905.

106. Electrolytic solution pressure.—It is possible from the potential difference between a metal and its salt solution to calculate the solution pressure in atmospheres. The equation is

$$\pi = \frac{RT}{n_v \varepsilon_0} \log_e \frac{P}{p},$$

or at 17°

$$\log P = \frac{\pi n_v}{0.0002T} + \log p.$$

If we use normal solutions, p is equal to $22.4 \times \frac{290}{273}$ atmospheres if completely dissociated, The pressure of the ions, in case the salt is not completely dissociated, is then easily found (i.e., $\alpha \times 22.4\frac{290}{273}$ atmospheres). Since π can be determined, the value for P can be found for all metals. In the table on page 458 the values in atmospheres, as determined by Neumann, are given:

These values it must be remembered are merely symbolical, for the gas laws may not be applied to such an extent. The relation between these numbers, however, are the experimentally determined relative effects of the metals, as a glance at the formula will show.

TABLE XVIII.

SOLUTION PRESSURES OF METALS.

Zinc	9.9×10^{18}	atmospheres
Cadmium	2.7×10^{6}	“
Thallium	7.7×10^{2}	“
Iron	1.2×10^{4}	“
Cobalt	1.9×10^{0}	“
Nickel	1.3×10^{0}	“
Lead	1.1×10^{-3}	“
Hydrogen	9.9×10^{-4}	“
Copper	4.8×10^{-20}	“
Mercury	1.1×10^{-16}	“
Silver	2.3×10^{-17}	“
Palladium	1.5×10^{-36}	“

The influence of the dilution on the difference of potential depends upon the magnitude of the electrolytic solution pressure. If the latter is great, dilute solutions are necessary for maximum action; if small, more concentrated solutions are to be preferred.

107. Cells with inert electrodes.—Elements of this type have electrodes in solutions which do not contain the ions of the electrodes. Such cells are also known as *oxidation and reduction cells.* An example is given by the arrangement

$$\text{plat.Pt} - FeCl_3\text{sol.} \ldots\ldots SnCl_2\text{sol.} - \text{plat.Pt.}$$

$Sn^{\cdot\cdot}$ ion goes over into the $Sn^{::}$ ion, taking up the tricity set free by the transformation of $Fe^{\cdot\cdot\cdot}$ ion into . The Fe side, then, is positive and the Sn side ıtive.

he current in these cells is due to the oxidation the one side and the reduction on the other. An lizing substance (i.e., one which is reduced) is substance from which negative ions are formed or n which positive ions give up their charges. A ıcing substance is one in which negative ions are n up or positive ions formed.

)8. Processes taking place in the cells in common —All cells give an E.M.F. which is equal to the rence of the differences of potential at the two single rodes; but in many cases the action is complicated ther processes. In the following the effect of ›larizers is given, as well as the change in the cell ng action.

'ark cell.—This cell, as already mentioned, is used standard of E.M.F. The scheme is

$$Hg-Hg_2SO_4-ZnSO_4-Zn.$$

Hg_2SO_4 is not quite insoluble, therefore a small entration of $\dot{H}g$ ion does exist in the solution. The ion with its high solution pressure is driven ı the electrode into the $ZnSO_4$ solution, and forces re it to the electrode the $Hg^{\cdot}$ ion, since the solution can contain only the same concentration of positive as negative ions. The $Hg^{\cdot}$ ion gives up its charge to the electrode, which becomes positive, the Zn being negative from loss of positive ion. The current goes, then, externally through the wire from the Hg to the Zn, and internally from the Zn to the Hg. If the resistance placed against the cell is great enough, only an infinitesimal amount of $Hg_2^{\cdot\cdot}$ ion will be driven from the solution, and the cell remains constant. If the current is passed through a small resistance, however, all the $Hg_2^{\cdot\cdot}$ ion is soon precipitated upon the electrode and the E.M.F. is reduced, i.e., the cell is polarized. If allowed to stand, however, more Hg_2SO_4 will dissolve and the original E.M.F. is attained.

The Leclanché cell consists of a solution of ammonium chloride, in which we have two electrodes, Zn and $C+MnO_2$. The action of the MnO_2 is to prevent polarization, the processes taking place without it and with it being as follows:

In the cases without MnO_2 the Zn with its high solution pressure goes into solution, driving before it the other positive ion, i.e., $NH_4^{\cdot}$. This ion decomposes on losing its changes, forming NH_3 and H gases. The bubbles of H collect upon the electrode and are absorbed and so given off to the air, but as this process is slow, other ions are prevented from giving up their charges and consequently the E.M.F decreases. It is to get rid of this action of the H gas that the MnO_2 is used. In contact with water we have, then, to a small extent, a solution of MnO_2, which dissociates according to the scheme

$$MnO_2 + 2H_2O = Mn^{\cdot\cdot\cdot\cdot} + 4OH'.$$

This tetravalent Mn has the tendency to go into the divalent state by giving up two equivalents of electricity, i.e., to form the ion $Mn^{\cdot\cdot}$. In consequence of this the $Mn^{\cdot\cdot\cdot\cdot}$ ion with that of $NH_4^{\cdot}$ is driven to the electrode by the $Zn^{\cdot\cdot}$ ion, and, since it gives up two equivalents of electricity more readily than any other ion gives up its entire charge, the electricity is given up without any substance which might cause polarization. We have, then, $MnCl_2$ (i.e., $Mn^{\cdot\cdot}$ ion) formed in the solution. The process continues so long as there is solid Zn or MnO_2 present.

Bichromate cell.—This cell is arranged according to the scheme

$$Zn - H_2SO_4 + K_2Cr_2O_7 - C.$$

The action of the two substances in solution forms bichromic acid ($H_2Cr_2O_7$). This dissociates into

$$2H^{\cdot} + Cr_2O_7''$$

to a large extent, and to a smaller degree as follows:

$$H_2Cr_2O_7 + 5H_2O = 2Cr^{\cdot\cdot\cdot\cdot\cdot\cdot} + 12 \cdot OH'.$$

This hexavalent Cr has the tendency to give up three equivalents of electricity and to go into the trivalent state (i.e., $Cr^{\cdot\cdot\cdot}$). Accordingly the $Zn^{\cdot\cdot}$ ion which is forced from the electrode drives before it the $C^{\cdot\cdot\cdot\cdot\cdot\cdot}$ ion, which gives up three of its equivalents and become $Cr^{\cdot\cdot\cdot}$, remaining as such in the solution as ion in equilibrium with SO_4'' ion (i.e., as $Cr_2(SO_4)_3$). Finally, then, we have a solution of $Cr_2(SO_4)_3$ left in the jar. This change in the number of electrical equivalents by a change of valence always takes place more readily than the change from the ionic to the elemental state, and is of great value as a means of preventing polarization.

Accumulators.—The action of the lead accumulator or storage-cell also depends upon a change of valence. Any reversible cell can be recharged after it is used up by the passage of a current through it in the direction opposite to that in which it goes of itself. The lead cell, however, is generally used for the purpose owing to its high E.M.F. Before charging it consists of two lead plates, one of which is coated with litharge (PbO) in a 20% solution of sulphuric acid. If the current is passed through these plates (the PbO being positive), the PbO is transformed into PbO_2, lead superoxide (or supersulphate), while spongy lead is deposited upon the other electrode. The flow of current is now stopped, and the cell is charged.

The PbO_2 is soluble to a small degree and ionizes as follows:

$$PbO_2 + 2H_2O = Pb^{\cdot\cdot\cdot\cdot} + 4OH'.$$

This tetravalent Pb has the tendency to give up two of its electrical equivalents and to go into the divalent form. Since this is true, the Pb electrode must have the higher solution pressure, and the ion formed from it will drive the $Pb^{\cdot\cdot\cdot\cdot}$ to the electrode, where it will lose two charges of electricity and become divalent. This will continue as long as PbO_2 is present, i.e., until it is all transformed into the divalent state, $PbSO_4$. Other theories, by Liebenow and others, have also been advanced to explain this cell, but the reader must be referred elsewhere for them (see Dolezalek and von Ende, The Theory of the Lead Accumulator).

Dolezalek has been able to calculate the value of such a cell from the concentration of acid and the vapor-pressure of the solution, and finds an excellent agreement between theory and experiment. This proves the process, according to him, to be a primary one such as the theory of Le Blanc and that of Liebenow would make it.

D. ELECTROLYSIS AND POLARIZATION.

109. Decomposition values.—We must now consider the processes which take place when a current is passed through a solution from electrodes which are not affected by the liquid, i.e., inert ones, as platinum, gold, carbon, etc. The current causes the deposition of the positive and negative ions on the electrodes. If the primary current is disconnected at any time and the poles of the decomposition-cell connected with a galvanometer, we observe a current in the opposite direction which becomes weaker and weaker, until it finally disappears entirely. This is called the *current of polarization*, and its E.M.F. is the *E.M.F. of polarization*. This is caused by the tendency of the substance precipitated upon the electrode to go back into solution in the dissociated form.

It has been found that a certain minimum of E.M.F. is necessary to cause the steady electrolysis of any solution. If the E.M.F. used is smaller than this, the current goes through for an instant and then ceases; but at this point or above it the process goes steadily. This was found by Le Blanc, who determined the minimum values for a large number of liquids and solutions. The table below gives these values for molar solutions of the salts which separate metals.

TABLE XIX.

DECOMPOSITION VALUES FOR SALTS.

$ZnSO_4$	= 2.35 v.	$Ag(NO)_4$	= 0.70 v.
$Cd(NO_3)_2$	= 1.98 v.	$CdSO_2$	= 2.03 v.
$ZnBr_2$	= 1.80 v.	$CdCl_2$	= 1.88 v.
$NiSO_4$	= 2.09 v.	$CoSO_4$	= 1.94 v.
$NiCl_2$	= 1.85 v.	$CoCl_2$	= 1.78 v.
$Pb(NO_3)_2$	= 1.52 v.		

The values for $Cd(NO_3)_2$ and $CdSO_4$ show that those r the nitrates and sulphates of the same metal are arly the same.

The following tables contain the values for acids d bases. Here there is a certain maximum, which reached by many and exceeded by none, which is out 1.70 volts.

TABLE XX.

DECOMPOSITION VALUES FOR THE ACIDS.

Sulphuric	= 1.67 v.	Dextrotartaric	= 1.62 v.
Nitric	= 1.69 v.	Pyrotartaric	= 1.57 v.
Phosphoric	= 1.70 v.	Trichloracetic	= 1.51 v.
Monochloracetic	= 1.72 v.	Hydrochloric	= 1.31 v.
Dichloracetic	= 1.66 v.	Oxalic	= 0.95 v.
Malonic	= 1.72 v.	Hydrobromic	= 0.94 v.
Perchloric	= 1.65 v.	Hydriodic	= 0.52 v.

TABLE XXI.

DECOMPOSITION VALUES FOR THE BASES.

Sodium hydroxide	= 1.69 v. $n/4$
Potassium hydroxide	= 1.67 v. $n/2$
Ammonium hydroxide	= 1.74 v. $n/8$
Methylamine $n/4$	= 1.75
" $n/2$	= 1.68
" $n/8$	= 1.74

The alkalies and alkaline earths when combined with the largely dissociated acids, i.e., those with decomposition values of about 1.70 volts, show approximately the same value, viz., 2.20 volts. The chlorides, bromides, and iodides have lower values, which are independent of the alkali metal.

It will be observed that all the acids and bases with the maximum value give off hydrogen and oxygen upon electrolysis. Those with the lower values, which in more dilute solutions give off oxygen and hydrogen, also reach this maximum value. Thus for HCl at different dilutions we have:

DECOMPOSITION VALUES FOR HCl.

Concentration.	π	Concentration.	π
2 normal	= 1.26	1/16 normal	= 1.62
1/2 "	= 1.34	1/32 "	= 1.69
1/6 "	= 1.41		

At the dilution $n/32$ H and O are given off instead of H and Cl, as at the strength of 2 normal, and the maximum is reached.

All the above results are for platinum electrodes. For gold the values are slightly different, but the relation remains the same.

110. Theory of polarization.—The process taking place upon an electrode during electrolysis has been studied by Le Blanc, who has been able to make the action quite clear. He measured the difference of tential between the cathode and its solution after the ssage of the current, varying the E.M.F. from 0 up to : decomposition value of the solution. At the denposition value he found the potential difference to the same as that exhibited by the solution in which ›laced a stick of the metal. Thus a molar solution of SO_4 is decomposed steadily at 2.03 volts, at which difference of potential between the cathode and ıtion is found to be +0.16 volt. A stick of cadım in a normal solution of $CdSO_4$ gives an E.M.F. al to +0.16 volt, i.e., the metal is negative. For ıe solutions this difference of potential between :trode and solution is found to be given without maximum being reached. This is true for $AgNO_3$, ch decomposes at 0.70 volt. The reason for this ıe negative solution pressure of the Ag, which causes ; to be deposited upon the metal, even without the rent.

Vhen an indifferent electrode is placed in a salt solu- ı, a small amount of ion must precipitate upon it; .erwise, from the equation

$$\pi = \frac{RT}{n_\gamma \varepsilon_0} \log_e \frac{P}{p},$$

vill be infinite, since $P = 0$; and if that is true it would possible to arrange a perpetual motion. Metal ion will then separate upon the electrode until the tendency for the deposited metal to go into solution in the ionic form just compensates the separating force. In this way the electrode will be charged positively, and the solution negatively, so that there will be between them a certain difference of potential. The value of this difference will depend upon the amount of metal upon the electrode, and will not necessarily be as large as that for the massive metal (compare with concentration of H in a platinum-black electrode). If we now connect the cell with a primary cell at a low E.M.F., more metal will be deposited, but this will increase *P*, so that no more deposition will take place at that E.M.F. If the potential is then increased, *P* will again increase and further deposition will be prevented. Finally, when the E.M.F. used is such that *P* receives its maximum value, i.e., that which the massive metal possesses, then the deposition will take place steadily. Here we assume the osmotic pressure of the metal ions to remain constant. For strong currents this is not true; it decreases, and hence the deposition becomes more and more difficult and the potential difference at the cathode increases. It is not difficult, however, to keep the value constant for a short time, and thus to find the difference of potential at the cathode.

At the same time that this takes place negative ion is separated upon the anode and the process is exactly logous. If oxygen is the gas which separates, its centration increases until the maximum is reached *P*) and the gas is given off in the air.

From the above it is possible to understand why a tain minimum E.M.F. is required to cause a steady ctrolysis. The separation takes place only when concentration of ions around the electrodes reaches aximum, i.e., not until the osmotic pressure exerted them is great enough to overcome the solution prese of the metal. From the case of $AgNO_3$ it would m that this maximum of concentration need not reached on both sides at the same time. The nature the electrodes, so long as they are of an inert subnce, has no influence except for gases, and then in following way: The cell platinized Pt+H gas H_2SO_4 − O gas + platinized Pt gives an E.M.F. of 7 volts. If 1.07 volts are passed through the cell the opposite direction, then we shall have equilibrium. smaller than this, H_2O is formed at the electrodes m the gas in the electrode and the ions in the solun. If larger than 1.07, H and O are given off from e electrodes. We have here the gas-cell which gives e value 1.07 decomposing water, and reversing at .08. When polished platinum electrodes are used for e decomposition, however, 1.68 volts are necessary for eady electrolysis, the difference between the 1.68 and e 1.07 being 0.6 volt. The difference in these two values is assumed to be due to the different ion which is separated in the two cases. Water may be considered as dissociated as a dibasic acid:

$$H_2O = H^{\cdot} + OH',$$
$$OH' = H^{\cdot} + O''.$$

At the value 1.08 volts the O″ ion present separates, causing water to decompose for a time and then as they are used up the process ceases. The 1.07 volts of the gas-cell are due to this ion O″, for the platinum-black gives it up to the solution in that form after having absorbed oxygen gas. When OH′ ion separates it reacts to form H_2O and O,

$$4OH' = 2H_2O + O_2,$$

and the force necessary to do this is 1.68 volts. Where the concentration of OH′ ion is great, in bases for example, the O″ ion would be present to a greater extent than in acids, and the decomposition at 1.08 should be more marked than with acids, as it is found to be. HCl has too small an amount of OH′ and O″ ions to carry any amount of current, so that in strong solutions Cl separates at 1.31 volts, at which point water cannot be decomposed into hydrogen and oxygen.

If we have in a decomposition vessel one large platinized electrode and one very small pointed one and use the latter as cathode, the large one as anode, we get a rapid decomposition of water at 1.1 volts, H being given off at the point, the oxygen being absorbed in the platinum black. We get then a reversal of the gas-battery. Using the point as anode, we get bubbles of oxygen first at 1.68 volts, H being absorbed by the large electrode. An example of the use of such a process is the Hildburgh cell (J. Am. Chem. Soc., 22, 300, 1900), which rectifies an alternating current. If the value of the alternating current is below 1.68, current can go through when the point is the cathode and is stopped when this is the anode, as it is by the next reversal; so that we get from this a current made up of a series of impulses all in the same direction instead of the alternating current which entered. A current of large voltage can then be rectified by passage through a series multiple of such cells.

111. Primary decomposition of water.—The E.M.F. of decomposition of a cell giving off hydrogen and oxygen is dependent upon the concentration of the two ions $H^{\cdot}$ and OH', but independent of the nature of the electroltye. The E.M.F. is the same for acids and bases so long as only H and O are separated. Since by the law of mass action the product of $H^{\cdot}$ and OH' ions in a solution must always be the same, it follows that for all electrolytes, since the E.M.F. of the cell must be the sum of those of the two electrodes, the minimum value must be the same for all substances which give off H and O. With the exception, then, of solutions of metallic salts, which are decomposed by H, and the chlorides, bromides, and iodides, which are decomposed by O, the ions of water only are the factors in the decomposition of solutions, and not those of the dissolved salt. Excluding those solutions mentioned above, then, all *solutions when electrolyzed show primary decomposition of water*. The current is conducted by all the ions in the solution. At the electrodes, however, that process takes place which requires the smallest expenditure of work, and that is the separation of H and O as gases. In the case of the electrolysis of K_2SO_4 in solution, when the current is not too strong, there is no necessity for assuming that the $K^{\cdot}$ and SO_4'' ions are separated upon the electrode and then redissolved. They simply collect around the electrode, but, as the H and O separate more easily, these are forced out. With a stronger current, of course, it is possible to cause the separation of K and SO_4, for then the $H^{\cdot}$ and OH' ions, being present to but a small extent, cannot carry all the current, and the work of separation of the ions of the salt is smaller than that necessary to remove the very much diminished amount of OH' and $H^{\cdot}$. The formation and decomposition of H_2O are reversible processes, so that there is no loss of work connected with them, while with the secondary action there would be. The $H^{\cdot}$ and OH' ions are formed as they are used up, i.e., more water dissociates.

All bases and acids must have the same E.M.F., for the product of the $H^{\cdot}$ and OH' ions is always the same. For salts we should obtain a higher value, since upon the electrode at which H separates a base is formed, and OH' ion increases in amount, driving back that of $H^{\cdot}$, so that the difference of potential on that electrode increases, i.e., P remains the same, while p decreases. On the other electrode $H^{\cdot}$ ion collects and exerts the same decreasing effect upon the OH' ion. The smaller the dissociation of the base and acid formed the smaller naturally this influence will be.

In the case of HCl ($n/1$), Cl gas is given off steadily at a smaller E.M.F. than for the oxygen acids. As the acid becomes more dilute, however, the amount of $H^{\cdot}$ and Cl' ions decreases, until finally there is such a large concentration of OH' ions present, as compared with that of Cl', that O separates the more readily. This explains the results already given for HCl in different dilutions.

112. Electrolytic separation of metals by graded electromotive forces.—As we have seen, the salts of the different metals have different decomposition values. From this fact Freudenberg * showed how it is possible to separate metals quantitatively. It is only necessary pressures of the ions $Ag^{\cdot}$ and $H^{\cdot}$. We have then, taking the decomposition value of $H^{\cdot}$ as zero and that of $Ag^{\cdot}$ as -0.78 (since, when $p_1 = 1$, $0.0575 \log P_1 = -0.78$),

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* Zeit. f. phys. Chem., 12, 97, 1893.

$$\pi = 0.0575 \log \frac{P_1}{p_1} = 0.0575 \log P_1 - 0.0575 \log p_1$$
$$= -0.78 - 0.0575 \log p_1.$$

p_1, however, the concentration of $Ag^{\cdot}$ ions, can only reach a certain value in the presence of Cl, Br, and I, which value is regulated by the solubility products of AgCl, AgBr, and AgI. The solubilities at 25° are respectively 1.25×10^{-5}, 6.6×10^{-7}, and 0.97×10^{-8}. If I is present in the ionic state to the concentration 0.1 mole per liter, $p_1 = \frac{(0.97 \times 10^{-8})^2}{0.1}$, from which $\pi_1 = +0.09V$, i.e., the system acts as a cell and gives a current, Ag dissolving and H being evolved. For Br, $\pi = -0.12V$; and for Cl, $\pi = -0.2V$. If I' ions are reduced in concentration to 0.0001 mole per liter, π becomes -0.084. In this way, by varying the E.M.F., the iodide and then the bromide are transformed into the silver salt, and the difference in weight of the anode before and after the experiment gives the weight of the one which has been separated. Cl is usually determined by titration after the Br and I have been removed.

CHAPTER X.

PROBLEMS.

(*These answers were obtained by use of a four-place logarithm table.*)

ENERGY.

1. How many ergs are equivalent to 3.52 (18°) calories? *Ans.* 147,241,600 ergs.

2. What velocity will a force of 2.12 dynes acting for seconds upon a body weighing 3.62 grams give the ody? *Ans.* 1.17 cm. per second.

3. The velocity of a body weighing 1.23 grams is 4.3 m. per second, what force has acted upon it for one econd? *Ans.* 5.29 dynes.

4. What is the pressure in dynes per sq. cm. of 21 mm. of Hg? *Ans.* 961,000.

THE GASEOUS STATE.

5. An open vessel is heated to 819° C. What portion of the air which the vessel contained at 0° remains in it? *Ans.* 0.25.

6. An open vessel is heated until one-half of the gas

contained at 15° is driven out. What is the temperature of the vessel? *Ans.* 303° C.

7. A volume of gas, measured at 15°, is 50 cc. At what temperature would its volume become 44 cc.? *Ans.* −19°.6 C.

8. A volume of gas at 766 mm. pressure is 137 cc. What would it be at 757 mm.? *Ans.* 138.7 cc.

9. What volume does 1 mole of gas occupy at 50°, the pressure being 760 mm.? At 100°, p being 900 mm.? *Ans.* 50° = 26.5, at 100° = 25.8 liters.

10. A volume of air in a bell jar over water measures 975 cc. The water in the jar is 68 mm. above the water in the trough, and the barometer stands at 756 mm. What would the volume be if exposed to standard pressure, the specific gravity of Hg being 13.6? *Ans.* 963.4.

11. At 14° C. and 742 mm. pressure a volume of gas measures 18 cc. What will be its volume at 0° and 760 mm. pressure? *Ans.* 16.72.

12. A volume of H at a temperature of 15° measures 2.7 liters, with the barometer at 752 mm. What would have been its volume had the temperature been 9°, and the pressure 762 mm.? *Ans.* 2.6 liters.

13. What volume is occupied by 44 grams of oxygen at 70 cm. pressure and 35° C.? *Ans.* 37.7 liters.

14. $\frac{1}{2}$ mole of H, $\frac{1}{2}$ mole of O, and $\frac{1}{3}$ mole of N are mixed in a volume of 10 liters at 0° C. What are the partial pressures of H, O, and N?

Ans. $p_H = 1156.96$, $p_O = 1156.96$, and $p_N = 771.65$ grams per sq. cm.

15. What would these pressures (14) be in atmospheres at 10° C.?

Ans. $p_H = 1.164$, $p_O = 1.164$, and $p_N = 0.774$.

16. 1 liter of N weighs 1.2579 grams at 0° and 760 mm. Calculate the specific gas constant, r.

Ans. 3007 gr. cm.

17. The specific gas constant, r, for N was found above (16). What is it for H? Atomic weight of N s 14.01, and of H is 1.008. *Ans.* 41,800 gr. cm.

18. How much will 100 liters of chlorine at 74 cm. pressure and 30° C. weigh? *Ans.* 278.7 grams.

19. 1 gram of a gas occupies 339.7 cc. at 100° and atmospheric pressure. What is its molecular weight?

Ans. 78.

20. A solid gives off a gas which is dissociated to 41%, into two products. What is the work done, in calories, gram-centimeters, and liter-atmospheres, when 1 mole of solid goes into the gaseous state, the temperature of dissociation being 55° C.?

Ans. 925 cals., 39,410,000 gr. cm., 37.96 L. A.

21. How much work will be done by 1 kg. of CO_2 when heated 200°? In other words, what is the difference in the amount of work when the 1000 grams of CO_2 are produced from the negligible volume first at $T + 200$, and then at T? *Ans.* 373.1 L. A.. 9088 cals.

22. The time necessary for CO_2 to flow through a small opening is 26.5 minutes. Under the same conditions the time for H is 5.6 minutes. Find the density of CO_2. *Ans.* 22.3

23. The time of outflow of a gas is 21.4 minutes, the time for hydrogen is 5.6 minutes. Find the molecular weight of the gas? *Ans.* 29.2.

24. The density of a gas is 2.786 referred to N (mol. w'g't = 28). What is its molecular weight? *Ans.* 78.

25. The density of a gas is 0.23 referred to gaseous Hg (mol. w'g't = 200). What is its molecular weight? *Ans.* 46.

26. H is at the partial pressure of 2.136 atmospheres in a space of 10 liters. How many moles per liter are there, the temperature being 0°? How many moles in the 10 liters? *Ans.* $c = 0.0954$; 0.954.

27. Starting with 1 mole of A in 22.4 liters (at 0°, 760 mm.), assume the dissociation according to the scheme $A = 2B + 3D$ (here A, B, and D represent moles) to be 23%. What will be the final volume, where pressure and temperature remain unchanged? *Ans.* 43 liters.

28. What is the final concentration of A, B, and D in (27)?

Ans. $A = 0.0179$, $B = 0.0107$, and $D = 0.01604$ moles per liter.

29. The molecular weights in (27) are $M_A = 170$,

$M_B=25$, and $M_D=40$. How many grams per liter are there of each at equilibrium?

Ans. $A=3.04$, $B=0.268$, and $D=0.642$.

30. Assume in the reaction $A=2B+3D$ that we start with 17 grams of A ($M=170$) in 2.24 liters (0°, 760 mm.). Find concentrations, partial pressures and grams per liter of A, B, and D, where the dissociation of A is 20% ($M_B=25$, $M_D=40$), and the volume and temperature remain constant. What is the total pressure of the system?

Ans. $A=0.036$, $B=0.018$, $D=0.027$ moles per liter.
$A=6.12$, $B=0.45$. $D=1.08$ gr. per liter.
$A=0.8$, $B=0.4$, $D=0.6$ atmospheres.
Total pressure $=1.80$ atmospheres.

31. Starting with 0.1 mole of A at 75°, knowing the dissociation to be 32%, according to the scheme $A=2B+D+2E$, find concentrations and partial pressures of A, B, D, and E at equilibrium (*a*) when the volume increases under constant, atmospheric, pressure; (*b*) when the volume remains constant at what it was for the 0.1 mole of A alone.

Ans. (*a*) $c_A=0.00916$, $c_B=0.0086$, $c_D=0.0043$, and $c_E=0.0129$ moles per liter.
$p_A=0.262$, $p_B=0.246$, $p_D=0.123$, and $p_E=0.369$ atmospheres.
(*b*) $c_A=0.0238$, $c_B=0.0224$, $c_D=0.0112$, and $c_E=0.0336$ moles per liter.

$p_A = 1.945$, $p_B = 1.826$, $p_D = 0.913$, and $p_E = 2.739$ atmospheres.

32. In the reaction $A = 2B + D$, A is a solid which practically does not exist as a gas, and B and D are gases. At 100° the dissociation pressure of A (i.e., of the gases A and B produced from A) is 2 atmospheres. Find the partial pressures and concentrations in moles per liter of B and D.

Ans. $p_A = 0$, $p_B = 2/3 \times 2$, and $p_D = 1/3 \times 2$ atmospheres
$c_A = 0$, $c_B = 0.0436$, and $c_D = 0.0218$ mole per liter.

33. When heated PCl_5 dissociates into PCl_3 and Cl_2. The molecular weight of PCl_5 is 208.28. At 182° the density is 73.5, and at 230° it is 62. Find the degree of dissociation at 182° and 230°.

Ans. $\alpha_{182°} = 41.7\%$, $\alpha_{320°} = 68\%$.

34. Sulphur, S_8, dissociates under certain conditions into the form S_2. If this dissociation were complete, what would be the density of the gas, S_2, referred to chlorine (mol. w't'g = 71)? *Ans.* 0.9014.

35. The ratio of the specific heat for constant pressure to that for constant volume is equal to 1.67 for helium. How many atomic weights are there in the molecular weight?

36. How many atomic weights are there in the molecular weight of argon, the specific heat for constant volume being 0.075? The density gives the molecular weight of 40. *Ans.* 1.

37. What is the specific heat of CO_2 gas at constant volume, i.e., c_v? The molecular weight is 44 and the temperature is 50°. *Ans.* 0.164.

38. The time of outflow through a small opening is found for a di-atomic gas to be 22.3 minutes; for H it is 5.6. What is its specific heat for constant volume?

Ans. 0.153.

39. The specific heat for constant pressure, c_p, of benzene is 0.295, what is the specific heat for constant volume, c_v? *Ans.* 0.27.

40 The specific heat, c_v, of CO_2 is 0.2094; what is the ratio of that for constant pressure to that at constant volume? *Ans.* $\frac{c_p}{c_v}=k=1.22$.

41 CO_2 gas, for which k was found in (35), is compressed in a flask to the pressure 1.5 atmospheres, and this pressure allowed to equalize rapidly against the atmospheric pressure, equal to 760 mm. What is the temperature produced? The original temperature was 0° C. *Ans.* $-19°.2$ C.

42 Air ($k=1.4$) compressed to pressure equal to 50 atmospheres, is expanded rapidly to double its initial volume against the pressure of the atmosphere. What temperature is produced by the expansion? The original temperature was 0° C. *Ans.* $-66°.1$ C.

What effect has the original pressure here?

43 Two gases, $k_1=1.4$, $k_2=1.22$, are compressed

rapidly, each to $\frac{1}{10}$ of its original volume. What temperatures are produced if 0° is the initial one?

Ans. $t_{k_1}=412^\circ.8$, $t_{k_2}=180^\circ.1$ C.

44. A mixture of hydrogen and oxygen gases is compressed rapidly (adiabatically) from the volume 40.1 cc. to 3.04 cc., the temperature rising from 20° to 549° C. What is the value $\frac{c_p}{c_v}$ for the gaseous mixture? *Ans.* 1.4.

45. A mixture of gas is compressed rapidly (adiabatically) from the pressure 1.74 atm. to 64.3 atm., the initial temperature is 20° and $\frac{c_p}{c_v}=1.4$. What is the final temperature? *Ans.* 549° C.

46. The volume of a mixture of gases is changed rapidly (adiabatically) from 227.8 cc. to 18.85 cc., $\frac{c_p}{c_v}=1.4$ and the initial pressure is 1.25 atm. What is the final pressure? *Ans.* 40.8 atm.

THE LIQUID STATE.

47. A volume of 50 liters of air in passing through a liquid at 22° causes the evaporation of 5 grams of substance, the molecular weight of which is 100. What is the vapor-pressure of the liquid in grams per square centimeter? *Ans.* 25.

48. The vapor-pressure of a substance is 44 mm. at 20° C., and its molecular weight is 46. How many

ns of liquid will evaporate when 100 liters of air pass
ugh? *Ans.* 11.08.

9. Calculate the critical temperature of a mixture
aining 63.96 parts by the weight of ether and 36.04
enzene. The critical temperature of ether is 193°.5,
enzene 296°.4. *Ans.* 230°.7; Exp. = 231°.4.

0. *n*-hexane ($M = 85.82$) has a molecular volume in
gaseous state equal to 34,500 c.c., that in the liquid
e being 137.96; both being measured at 60° C.
at is the latent heat of evaporation of 1 gram of *n*-
ane? *Ans.* 85.7 cals.

1. For CO_2 at 0° we have the following values:
sity in liquid state 0.905, density in gaseous state
9. What is the latent heat of evaporation of 1 gram
quid CO_2? *Ans.* 54.9. Observed is 57.48.

2. The latent heat of evaporation of chloroform at
is 58.49 cals., the boiling-point is 61°, and the molec-
weight in gaseous form is 119.1. What is the for-
a of the substance in the liquid state?

3. The latent heat of methyl alcohol at its boiling-
it, 66°, is 267.48 cals., the molecular weight in gaseous
n being 32. Find molecular weight in the liquid form.
hat conclusion is to be drawn from this result?

4. The heat of evaporation of ether at 34°.5 is 88.39
. This is for one gram. Find the change in boiling-
nt due to a change from 760 to 634.8 mm.
Ans. −4°.76.

55. Find heat of evaporation of ethyl formate. $\frac{dp}{dT}=27$ mm., the boiling-point is 54°.3 at 760 mm., and the molecular weight is 74. *Ans.* 102.8.

56. Find $\frac{dp}{dT}$ for ethyl propionate. The heat of evaporation is 77 cals., the density in liquid form is 0.7958, and in the gaseous state 0.0033, both at the boiling-point, 99°. *Ans.* 21.5 mm.

57. The refractive index of liquid N is 1.2062, and for liquid air is 1.2053. Find that for liquid O. Air is composed by weight of 23.01% of O and 76.99% of N, $d_O=1.124$, $d_A=0.9673$, $d_N=0.885$. *Ans.* 1.16.

For further examples on refractive index see Maybery and Shepherd. (Am. Chem. Jour. 29, 278, 1904.)

58. c_v for gaseous benzene (C_6H_6) at 50° is 0.269; for liquid benzene at the same temperature $c=0.4502$. What is the change in the heat of evaporation per degree around 50°? *Ans.* 0.1552 cal. per degree.

59. What is the heat of evaporation of ether at 80° if the external pressure is increased so as to increase the boiling-point from 35° to 80°? Specific heat of liquid at 80° is 0.690, molecular weight is 74, and heat of evaporation at 35° is 88.39 cals. (see data in text). *Ans.* 77.14 cals.

60. Find $\frac{\varDelta T}{\varDelta p}$ for ether at 80° as given in (59); the vapor-pressure of ether at 80° is 299.14 cm. *Ans.* 0.0146 per mm.

61. What change in external pressure is necessary to alter the boiling-point of ether in (59) from 35 to 80°?

Ans. 4.06 atmos.

62. 1 gram of liquid as a gas at 100° and 760 mm. occupies 413.5 cc. $\frac{c_p}{c_v}=1.097$. The heat of evaporation as liquid at 15°.5 is 89.25, and at 24°.83 is 84.5 cals. Knowing the molecular weight as a liquid to be the same as that in the gaseous state, find the specific heat as a liquid. At what temperature does this hold?

Ans. 0.5506; Exp. = 0.545. 25°.16.

63. The latent heat of evaporation of liquid NH_3 at its boiling-point, under atmospheric pressure (−33°.5), is 341 gram calories per gram. Is liquid NH_3 associated or non-associated?

64. The boiling-point, under atmospheric pressure of hexane (C_6H_{14}) is 69°. What is its latent heat of evaporation? It is non-associated.

Ans. 82.6; exp. 82.9 cals.

65. The boiling-point, under atmospheric pressure of *p*-nitrotoluene, is 237°.7, the latent heat of evaporation is 84 cals. What is the molecular weight in the liquid state? *Ans.* 137.

66. What is the change in vapor-pressure for ether (60) per degree? *Ans.* 68.5 mm.

67. What is the surface tension of C_6H_6 in dynes per centimeter? The radius of the capillary tube is 0.01843

cm. at 46° and the liquid ascends 3.213 cm., its density being 0.85. *Ans.* 24.7 dynes per cm.

68. Find height to which CS_2 will ascend in a capillary tube of a radius of 0.01708 cm., the surface tension being 27.68 dynes per centimeter, and the density 1.224. *Ans.* 2.7 cm.

69. Find the molecular weight of C_6H_6 as a liquid. The surface tension at 46° is 24.71 dynes, its critical temperature is 288°.5, $k=2.12$, and its density is 0.85. *Ans.* 78.

70. Find the molecular weight as a liquid of CS_2. Its surface tension (46°) is 29.41 dynes, its density 1.224, and its critical temperature 280°.3. *Ans.* 76.

71. At 14°.8 acetyl chloride (density = 1.124) ascends to a height of 3.28 cm. in a capillary tube of a radius equal to 0.01425 cm. At 46°.2, in the same tube, the height is 2.85 cm. and the density 1.064. Find the critical temperature of acetyl chloride ($M=78.5$). *Ans.* 235°.2.

72. From a certain tip the weights of a falling drop of benzene are 35.239 (11°.4, density = 0.888) and 26.530 (68°.5, density = 0.827) milligrams. The molecular weight is normal in the liquid state, i.e., 78. Find the critical temperature of benzene. *Ans.* 288°.4; exp. 288°.

73. From the same tip as was used in (72) the weights of a falling drop of chlorbenzene are 41.082 (8°.2, density

=1.12) and 32.054 (72°.2, densitv=1.0498) milligrams. What is the molecular weight of chlorbenzene as a liquid? What is its critical temperature?

Ans. 112.5; 359°.5; exp. 360°.

74. From the same tip as was used in (72) the weight of a falling drop of aniline at 51°.7 is 45.903 (density=0.9944) milligrams. What is the critical temperature of aniline? *Ans.* 425.8; exp. 426.

THE SOLID STATE.

75. The specific heat of Ni is 0.1092. What number should be selected as the atomic weight of Ni? *Ans.* 58.

76. The specific heat of Fe is 0.112. What number should be selected as the atomic weight of Fe?

Ans. 56.6.

77. The specific gravity of solid phenol is 1.072, and in the liquid state it is 1.0561; the latent heat of fusion is 24.93, and the melting-point is 34°. Find variation in the melting-point due to a change in pressure of one atmosphere. *Ans.* $\frac{\Delta T}{\Delta p}=0^{\circ}.00421$ per atmos.

78. Acetic acid melts at 16°.6 C., $\frac{\Delta T}{\Delta p}=0^{\circ}.0242$ per atmos., the heat of fusion is 46.42 cals. Find change in volume by the liquefaction of 1 gm. *Ans.* 0.00016 liter.

79. Specific heat of solid acetic acid is 0.4599 from 10°–15°, of liquid is 0.5026. Find heat of fusion at 50° from that at 5°.6, which is 44.34 cals. *Ans.* 46.24 cals.

0.0148 of N, the pressure of each being that of the atmosphere. What is the composition of air absorbed in H_2O?

Ans. 34.8% by volume of O and 65.2 of N.

92. What would be the composition of the air if that dissolved in (91) were collected and re-dissolved in fresh water? *Ans.* 51.9% by volume of O, and 48.1 of N.

93. Find molecular weight of naphthalene; 49.4 grams of H_2O and 8.9 grams of naphthalene go over when distilled at 98°.2 and 733 mm. from the system of immiscible liquids. The vapor-pressure of H_2O at 98°.2 is 712.4

Ans. 112.

94. The molecular weight of H_2O is 18, of nitrobenzene is 121. Vapor-pressure at 99° (the boiling-point of the immiscible liquid system) of pure H_2O is 733 mm., and of nitrobenzene is 27 mm. How much nitrobenzene is contained in the distillate?

Ans. 0.2 of total by weight.

95. What is the surface energy involved on a cubic centimeter of gypsum powder (2.5 grams) when it is reduced to cubical particles with an edge equal to 0.0001 mm. and added to water? The surface tension of water is 80 dynes. *Ans.* 4.8×10^7 ergs.

96. What is the osmotic pressure of a 1% solution of glucose ($M=180$) at 0° C.?

Ans. 94.6 cm. H; Exp. = 94 cm.

97. The osmotic pressure of a solution of cane-sugar

0° is 49.3 cm. of Hg. What percentage of sugar =342) is contained in it? *Ans.* 0.99%; Exp.=1.0%.

8. The osmotic pressure of a sugar solution at 32° C. 4.4 mm. What is it at 14°.2? *Ans.* 51.2 mm.

9. The osmotic pressure of solution containing 10 ns of sugar to a certain volume is 200 mm. What hat for the same volume containing 13.5 grams?

Ans. 270 mm.

00. 1 mole of sugar (342 grams) is dissolved in 1 liter vater. Find osmotic pressure at 22°.45.

Ans. 24.3 atmos; Exp. 24.5.

01. 10.442 grams aniline in 100 grams of ether gives a or-pressure of 210.8 mm. Ether alone ($M=74$) gives .6. Find molecular weight of aniline. *Ans.* 87.

02. Find osmotic pressure at 0° of aniline in (101) in ospheres and grams per square centimeter. The sity of ether is 0.737.

Ans. 19.82 atmos. or 20,460 gr. per sq. cm.

03. The osmotic pressure of a substance in water solu- is 100 cms. at 0° C. Find the vapor-pressure of solution; that of water at 0° is 4.57 mm.

Ans. 4.56 mm.

04. What is the work, in gr.-cms. and calories, neces- y to separate by isothermal osmotic work 200 grams a substance ($M=60$) from the solvent at 20° C.? grams of substance to the liter of solvent.

Ans. 1953 cals.; 83,200,000 gr. cms.

105. 64.74 grams of propylene bromide ($M = 2222$) are mixed with 145.93 grams of ethylene bromide ($M = 206$) at 85°.05; the vapor-pressure of pure propylene bromide at this temperature is 127.2 mm., and that of ethylene bromide is 172.6 mm. What is the partial vapor-pressure of each in the mixture? What is the composition of the distillate? What is the total vapor-pressure of the mixture?

Ans. p' (ethylene bromide) = 122.3 mm.
observed = 121.4 "
p' (propylene bromide) = 37.1 "
observed = 37.3 "
total vapor-pressure = 159.4 "
observed = 158.7 "

24.6 grams of propylene bromide and 75.4 grams of ethylene bromide in each 100 grams of distillate. Observed values are 24.9 and 75.1.

106. The increase in the boiling-point of 54.65 grams of CS_2 caused by the addition of 1.4475 grams of P is 0°.486. What is the molecular weight of P in CS_2?

Ans. 129.2.

What is the formula, the atomic weight being 31?

107. Calculate the increase in boiling-point ($K_{b.p.}$) of ether when to 1000 grams we add a mole of a substance. The boiling-point of ether is 34°.97, the latent heat of evaporation is 88.39. *Ans.* 2°.15.

108. The boiling-point constant ($K_{b.p.}$) of H_2O, as

ised by the addition of 1 mole of substance to 1000
ms, is 0°.52. Find heat of evaporation of H_2O.
Ans. 535.1 cals. per gram.

09. At 40° the change of vapor-pressure per degree
benzene ($M=78$) is 0.881 mm. for a mean pressure
22.42 cm. What is the boiling-point constant ($K_{b.p.}$)
enzene under this reduced pressure? *Ans.* 1°.985.

10. 10 grams of a substance in 100 grams of a solvent
rease the boiling-point by 0°.87. The molecular
ght of the substance is 60. Find the boiling-point
stant ($K_{b.p.}$). *Ans.* 0°.522.

11. The increase of the boiling-point of a water
tion is 0°.21. What is the osmotic pressure at 100°?
$_{p.}$=0°.52. *Ans.* 12.36 atmos.

12. From (111) find the vapor-pressure of the
tion at 100°, that of pure water is 760 mm.
Ans. 754.6 mm.

13. 0.284 grams of the oxime $(CH_3)_2CNOH$ causes a
rease of 0°.155 in the freezing-point of 100 grams of
ial acetic acid. $K_{f.p.}$ for acetic acid is 3°.88. Find
molecular weight of the oxime. *Ans.* 71.

14. A normal water solution gives a depression of
, when the overcooling is 2.21. What is the strength
he solution whose freezing-point is observed?
Ans. 1.028 *N*.

15. Find the freezing-point depression of the normal
tion itself in (114). *Ans.* 2°.04.

116. Find the heat of fusion of nitrobenzene; its melting-point is $5^\circ.3$, the freezing-point constant $(K_{f.p.})$ is 7.07. *Ans.* 21.9 cals.

117. The specific heat of nitrobenzene is 0.3524, its heat of fusion is 21.9 cals. The observed depression of 10 grams of a substance in 72.5 grams of nitrobenzene is $1^\circ.21$ when the overcooling is 1°. What is the strength of the solution whose freezing-point is observed?

Ans. 140.2 grams per 1000.

118. Find the osmotic pressure at 46° of 1.4475 grams of P in 54.65 grams of CS_2. The molecular weight of P, in this solution, is 124, and the density of CS_2 is 1.2224.

Ans. 6.82 atmos.

119. Find the vapor-pressure in (118) of P in CS_2 solution at 0°, the vapor-pressure of CS_2 at 0° is 127.91 mm. *Ans.* 125.9 mm.

120. Find the osmotic pressure of 0.284 grams of the oxime $(CH_3)_2CNOH$ in 100 grams of glacial acetic acid at 17°. The density of acetic acid at 17° is 1.056.

Ans. 1 atmos.

121. What is the relation between the osmotic pressures of 0.01 mole of substance in 1000 grams of water and in 1000 grams of ether (sp. gr. = 0.7370), assuming the same molecular weight of the solute in each?

Ans. $P_e = 0.7370 P_w$.

122. Find the vapor-pressure of the solution of 0.284 gram of the oxime $(CH_3)_2CNOH$ in 100 grams of glacial

acetic acid at 40° C., the vapor-pressure of glacial acetic acid at 40° being 34.77 mm. *Ans.* 34.69 mm.

123. Find the molecular weight of KCl in molten $CaCl_2 \cdot 6H_2O$. 0.4212 gram of KCl in 60 grams of molten $CaCl_2 \cdot 6H_2O$ depress the freezing-point of this from 29°.48 to 29°.057. The heat of fusion of $CaCl_2 \cdot 6H_2O$ at its freezing-point is 40.7 cals. per gram. *Ans.* 75.

124. $K_{f.p.}$ for molten $LiNO_3 \cdot 3H_2O$ is 2°.6, its freezing-point being 29°.88. What is its heat of fusion?

Ans. 70.6 cals. per gram.

125. A 0.1 normal solution of acetic acid in water freezes 0°.1927 lower than H_2O. Find the degree of ionization of the acetic acid. *Ans.* $\alpha = 2\%$.

126. A .15 normal solution of succinic acid freezes 0°.2864 lower than H_2O. Find the ionization of the acid. *Ans.* $\alpha = 1\%$.

127. A 0.1 molar water solution of a substance is 32.4% ionized into three ions. What is its freezing-point ($K_{f.p.} = 1°.89$); its boiling-point ($K_{b.p.} = 0°.52$); its osmotic pressure at 28°; and its vapor-pressure at 0° (vapor-pressure of H_2O at 0° is 4.57 mm.)? The ionization is assumed here to remain the same at all temperatures.

Ans. Freezing-point $= -0°.3115$.
Boiling-point $= 100°.086$.
Osmotic pressure $= 4.07$ atmos.
Vapor-pressure $= 4.556$ mm.

128. From the values (obs.) for the ionization of KCl

(p. 324) calculate the ionization of 0.5 molar $BaCl_2$ into $Ba^{\cdot\cdot}$ and 2 $Cl^{\cdot}$. *Ans.* 56%.

129. What is the ionization of a 0.05 molar solution of $MgSO_4$ (into $Mg^{\cdot\cdot}$ and SO_4''). *Ans.* 53%.

130. A saturated aqueous solution of ether freezes at −3.85. When 4.76 grams of I are dissolved in 100 grams ether, a saturated aqueous solution freezes at −3.789. Find molecular weight of I in ether. The molecular increase of the freezing-point of water by the addition of 1 mole of substance to the ether is 3°.06 over that point for pure ether in water (see pp. 203, 204). *Ans.* 239.

THERMOCHEMISTRY.

131. Find the heat of decompositoin of $2H_2O$ into water from the following reactions:

$$SnCl_2 \cdot H_2Cl_2Aq + O = SnCl_4 \cdot Aq + H_2O + 657K;$$
$$SnCl_2 \cdot H_2Cl_2Aq + H_2O_2Aq = SnCl_4Aq + 2H_2O + 888K.$$

Ans. 231*K*.

132. The heat of combustion of NH_3 in O at constant volume and 18° is

$$2NH_3 + 3O = 3H_2O + N_2 + 1812K;$$

and

$$H_2 + O_2 = H_2O + 674.84K.$$

Find heat of formation of NH_3 from its elements.

Ans. 106.2*K*.

133. How does the heat of combustion of H with O

to form 18 grams of liquid H_2O at constant volume vary with the temperature? The heat capacity of 72 grams of H_2O is 0.72 K, and that of 4 grams of H plus 32 grams of O is 0.2056. *Ans.* $-.00772K$ per degree.

134. $CH_4+2O_2=CO_2+2H_2O+2119K$, $C+O_2=CO_2+970K$, and $H_2+O_2=H_2O+683.57K$, all at constant pressure and 18° C. Find heat of formation of CH_4.

Ans. $218.2K$.

135. Find heat of the reaction $H_2+2I=2HI$:

$$2KIAq+Cl_2=2KClAq+2I+524K.$$
$$HIAq+KOHAq=KIAq+H_2O+137K.$$
$$HClAq+KOHAq=KClAq+H_2O+137K.$$
$$2HI+Aq=2HIAq+384K.$$
$$2HCl+Aq=2HClAq+346K.$$
$$H_2+Cl_2=2HCl+440K.$$

Ans. $H_2+2I=2HI+112K$.

136. $K+Aq=KOHAq+H+481K$,

$$2H+O=H_2O+683.57K.$$

Find the heat formation of KOHAq from the elements. *Ans.* $1164.57K$.

137. $Zn+2HClAq=ZnCl_2Aq+H_2+342K$ at constant pressure. What is it for constant volume? Temperature is 20°. *Ans.* $347.9K$.

138. The following reactions take place:

$$C_6H_6+15O=6CO_2+3H_2O+yK$$

and

$$C_6H_6+15O=6CO_2+3H_2O+xK.$$

At 27°, assuming these to be at constant pressure, find values for constant volume.

139. Find the heat of the reaction

$$\mathrm{P}+3Cl=\mathrm{PCl_3},$$

$$\begin{aligned}
\mathrm{PCl_3+Aq} &= \mathrm{P(OH)_3Aq+3HClAq}+651K,\\
H_2+Cl_2+\mathrm{Aq} &= \mathrm{2HClAq}+786K,\\
\mathrm{2P}+3O_2+\mathrm{Aq} &= \mathrm{P(OH)_3Aq}+2504K,\\
2H_2+O_2 &= \mathrm{2H_2O}+683.2K.
\end{aligned}$$

Ans. $P+3Cl=\mathrm{PCl_3}+755.2K.$

140. Find the heat of formation of $\mathrm{H_2S_4O_6Aq}$.

$$\begin{aligned}
H_2+\mathrm{2I+Aq} &= \mathrm{2HIAq}+263K.\\
\mathrm{2Na_2S_2O_3Aq+2I} &= \mathrm{Na_2S_4O_6Aq+2NaIAq}+80K.\\
\mathrm{2NaOHAq+2HIAq} &= \mathrm{2NaIAq+2H_2O}+274K.\\
2H_2+O_2 &= \mathrm{2H_2O}+1368K.\\
\mathrm{4NaOHAq+2H_2S_2O_3Aq} &= \mathrm{2Na_2S_2O_3Aq+4H_2O}+594K.\\
\mathrm{2NaOHAq+H_2S_4O_6Aq} &= \mathrm{Na_2S_4O_6Aq+2H_2O}+271K.\\
\mathrm{4S}+2O_2+\mathrm{Aq} &= \mathrm{2H_2S_2O_3Aq}+1378K.
\end{aligned}$$

Ans. $H_2+\mathrm{4S}+3O_2+\mathrm{Aq}=\mathrm{H_2S_4O_6Aq}+2612K.$

141. Find heat of formation of HFAq.

$$\begin{aligned}
\mathrm{K_2SO_3Aq+2KOHAq}+2F &\\
&= \mathrm{K_2SO_4Aq+2KFAq+H_2O}+1280K.\\
\mathrm{2KOHAq+2HFAq} &= \mathrm{2KFAq+2H_2O}+326K.\\
\mathrm{2KOHAq+H_2SO_3Aq} &= \mathrm{K_2SO_3Aq+2H_2O}+290K.\\
\mathrm{H_2SO_3Aq}+O &= \mathrm{H_2SO_4Aq}+637K.\\
\mathrm{2KOHAq+H_2SO_4Aq} &= \mathrm{K_2SO_4Aq+2H_2O}+314K.\\
2H_2+\mathrm{O_2} &= \mathrm{2H_2O}+1368K.
\end{aligned}$$

Ans. $H_2+F_2+\mathrm{Aq}=\mathrm{HFAq}+2\times 488.5K.$

142. Find the heat of formation of $HClO_3Aq$.

$$2KClO_3 = 2KCl + 3O_2 + 194K.$$

$$KClO_3 + Aq = KClO_3Aq - 100K,$$

$$H_2O + KClO_3Aq = KOHAq + HClO_3Aq - 138K,$$

$$KCl + Aq = KClAq - 44K,$$

$$2H_2O + 2KClAq = 2KOHAq + 2HClAq - 276K,$$

$$2H_2 + 2Cl_2 + Aq = 4HClAq + 1572K.$$

Ans. $H + Cl + 3O + Aq = HClO_3Aq + 240K.$

143. What is the difference in energy between 18 grams of water at a 100° and water-vapor at the same temperature? Between water and ice at 0°? The latent heat of evaporation is 536.4, of fusion is 80 cals.

Ans. 9655 and 1440 cals.

144. Find heat of formation of gaseous hydrobromic acid from the reactions,

$$SO_2Aq + O = SO_3Aq + 63700 \text{ cals.},$$

$$2Br + SO_2Aq + H_2O = 2HBrAq + SO_3Aq + 54000 \text{ cals.},$$

when, in addition, we know that

$$H_2 + O = H_2O + 68400 \text{ cals.},$$

and

$$HBr = HBrAq + 20000 \text{ cals.}$$

Ans. $H + Br = HBr + 9350$ cals.

145. Find the heat of formation and heat of formation in solution of NH_3.

$$\left.\begin{array}{l} 2NH_3 + 3O = N_2 + 3H_2O + 181200 \text{ cals.} \\ 3H_2 + 3O = 3H_2O + 3 \times 68400, \end{array}\right\} \begin{array}{l} \text{const.} \\ \text{pressure.} \end{array}$$

$$NH_3 + Aq = 8400.$$

Ans. $(N, 3H) = 12{,}000$ cals.; $(N, 3H, aq) = 24{,}000$ cals.

146. $NaOH+50H_2O$ has a molecular specific heat equal to 885.0 cals. and SO_3+100H_2O that of 1797 cals. At 9°.16 these evolve 32,060 cals. by combining, and at 24°.42 they generate 31,650 cals. What is the specific heat (i.e., for 1 gram) of a solution of $Na_2SO_4+200H_2O$? *Ans.* 0.9603 cal.

147. At constant pressure and 18°

$$N_2O_4+H_2O+Aq = HONOAq+HONO_2Aq+155K.$$
$$H_2+2O_2+N_2+Aq=2HONOAq+616K.$$
$$H_2+3O_2+N_2+Aq=2HONO_2Aq+948K.$$
$$2H_2+O_2 = 2H_2O+1368K.$$

Find heat of the reaction

$$N_2O_4=N_2+2O_2+xK.$$

at constant volume and 8°. The specific heats per gram are 0.2438 cal. for N, 0.2175 for O, and 0.65 for N_2O_4, all at 18° and constant pressure.

Ans. $x=-39K$ at constant pressure and 18°.
$x=-35.1\ K$ at constant pressure and 8°.
$x=-46.34K$ at constant volume and 8°.

148. Find the heat evolved by the reaction

$$HCl+\tfrac{1}{2}O=\tfrac{1}{2}H_2O+Cl.$$

We know that

$$2H_2+O_2=2H_2O+115600 \text{ cals.},$$
$$H_2+Cl_2=2HCl+44000 \text{ cals.}$$

Ans. 6900 cals.

). What is the heat of formation of a very dilute on of magnesium chloride? (See text for data.)

Ans. 1875K.

CHEMICAL CHANGE.

ↄ. In the volume of 1 liter there are 0.14 mole of ↄgen and 0.081 mole of iodine. At the tempera- of 440° C.

$$K=\frac{p_1 p_2}{p^2}=0.02.$$

the amount o. hydriodic acid formed.

Ans. 0.14855 mole.

1. The initial pressure of I is 38.2 cm:, the fraction ng with H is 0.8. What is the original pressure e H? $K=0.02$. *Ans.* 40.35 cm.

2. At 279° and 737.2 mm. pressure α for the reaction $)_3=2NO+O_2$ is 0.13. Find K_p and K_c both for ·eaction as written, and also for 1 mole of NO_2, i.e., $O_2=NO+O$.

Ans. $K_p=0.00136$ for $2NO_2$; 0.0369 for NO_2.
$K_c=0.0000292$ for $2NO_2$; 0.0054 for NO_2.

3. At 440° in 50 liters we have a mixture of 2.74 :s of HI, 0.5 mole of H and 0.3011 mole of I. K 02. In which direction does the reaction go?

4. At 440° ($K=0.02$) 5.30 cc. of H are mixed with cc. of iodine-vapor. How much HI is formed?

Ans. 9.475 cc. Observed, 9.52 cc.

155. At 3000° and atmospheric pressure α for CO_2, according to the formula $2CO \rightleftarrows 4CO + O_2$, is equal to 0.4. What is the dissociation constant for 1 mole of CO_2 for partial pressures *Ans.* $K_p = \frac{p_{CO} p_{O}^{\frac{1}{2}}}{p_{CO_2}} = 0.2721$.

156. What is K_p (155) for 2 moles of CO_2?

Ans. $K_p = \frac{p^2_{CO} p_{O}}{p^2_{CO_2}} = 0.07406$.

157. At atmospheric pressure and 100° the gas A is 10.5% dissociated according to the scheme $A = B + D$. Find direction and extent of the reaction taking place when 1 mole each of A, B, and D are allowed to react under constant pressure at 100°.

Ans. 0.487 moles of A are decomposed, forming B and D.

158. The gas A is 15% dissociated ($A = B + D$) at 125°, the total pressure being 1.15 atmospheres. Find direction and extent of the reaction when the initial pressure of the three gases A, B, and D are respectively 0.5, 0.8, and 0.3 atmospheres.

Ans. 0.2577 atmosphere gain of A. Total final pressure = 1.418 atmospheres.

159. The gas A ($A = B + D$) is 50% dissociated at 125°, and constant, atmospheric, pressure. Find direction and extent of the reaction taking place when A, B, and D are present respectively at 0.1, 0.7, and 0.2 atmospheres at 125°, and constant, atmospheric, pressure.

Ans. 0.1 atmos. of A formed. Final vol. = 1.1 times original.

160. The gas A $(A = 3B + 2D)$ is 50% dissociated at 125° and constant, atmospheric, pressure. Find direction and extent of the reaction taking place when 0.1 atmosphere of A, 0.3 of B, and 0.6 of D are brought together at 125°, and constant, atmospheric, pressure.

Ans. A formed to the pressure of x atmospheres, the value of x being fixed by the equation

$$\frac{(0.027 - 0.81x + 8.1x^2 - 27x^3)(0.36 - 2.4x + 4x^2)}{(1 - 12x + 48x^2 - 64x^3)(0.1 + 0.6x - 4x^2)} = 0.08335.$$

Final volume is $(1 - 4x)$ times original volume.

161. The constant of equilibrium for the reaction of amylene and acetic acid is 830.1 (p. 265). At the temperature at which this is true 2 moles of amylene are mixed with a moles of acid in 2 liters, and 0.5 mole of ester is formed. Find a, the original number of moles of acid.

Ans. 0.5008 mole.

162. 6.63 moles of amylene with 1 mole of acid shows that 0.838 mole are formed in the total volume of 894 liters. How much will be found when we start with 4.48 moles of amylene and 1 of acid in the volume of 683 liters?

Ans. 0.8111 moles.

163. Acetic acid distributes between water and benzene so that in a certain volume of water we find 0.245 and 0.314 gram when in an equal volume of the ether layer we find respectively 0.043 and 0.071 gram. What is the

molecular weight of acetic acid in benzene? It is 60 water. *Ans.* 2.02×60.

164. After shaking 1000 cc. of a water solution of aniline with 59 cc. of benzene we find 0.03285 gram of aniline in 50 cc. of the benzene layer, and 0.0647 gram in 1000 cc. of the water layer. Find the coefficient of distribution of aniline. *Ans.* $\frac{c_{\text{water}}}{c_{\text{benzene}}}=0.099$.

165. (*a*) The solid *A* ($A=2B+3D$) has a dissociation pressure of 2 atmospheres at 100°, A practically existing only as a solid. Find the constant of the law of mass action (for pressures).

Ans. Constant = 1.106.

(*b*) Assume the solid A (165) to dissociate in a constant volume against a pressure of the gas *B* equal to 0.5 atmospheres at 100°. How much *D* will be formed?

Ans. x atmospheres; x being fixed by the equation

$$\tfrac{1}{4}x^3+\tfrac{2}{3}x^4+\tfrac{4}{9}x^5=1.106.$$

166. For $NH_4HS=H_2S+NH_3$, $K=62{,}400$ (for pressures in mm.) at 25°.1 C. In a vacuum at 25°.1 we introduce NH_3 and H_2S until we have a partial pressure of the former of 300 mm., and of the latter 594 mm. Then the reaction is allowed to take place. How much does each gas lose in pressure?

Ans. 157.2 mm.

167. For the reaction of the Deacon process for chlorine,

$$HCl+\tfrac{1}{2}O=\tfrac{1}{2}H_2O+Cl,$$

we find, since $\frac{1}{2}O=\frac{1}{4}O_2$, for

$$K_p=\frac{\sqrt{p_{H_2O}}\sqrt{p_{Cl}}}{p_{HCl}\sqrt[4]{p_O}},$$

the values 3.02 at 386° C. and 2.35 at 419° C. Calculate the heat evolved by the reaction under constant pressure.

Ans. 6942 cals. (Compare Problem 148.)

168. At 18°.4 1 mole of $BaSO_4$ dissolves in 50,055 liters at 37°.7 in 31,282 liters. On the justified supposition that $BaSO_4$ is completely ionized, find the heat of dissociation. *Ans.* −8836 cals.

169. The salt $Na_2HPO_4 \cdot 12H_2O$ has a vapor-pressure at 15° of 8.84 mm., at 17°.3 $p=10.53$ mm. Find the heat of vaporization, i.e., the heat change during loss of 1 mole of water of crystallization by evaporation.

Ans. −12,728 cals.

170. A mixture of alcohol and hydrochloric acid is an equilibrium in which a certain amount of H_2O is formed. At 77°, $K=0.307$, at 99°, $K=0.177$. Find the heat generated by the reaction. *Ans.* +6527 cals.

171. The speed constant of formation of HI from H and I is 0.00023; K, the equilibrium constant at that temperature, 374°, is 0.0157. What is the speed constant of decomposition? *Ans.* 0.0146. Obs. 0.0140.

172. To 1 liter of a molar solution of a monobasic acid ($K = 0.000018$), a salt with an ion in common, having an ionization at that dilution equal to 100%, is added. How much in moles in the dry state must be dissolved to decrease the concentration of $H^{\cdot}$ ion of the acid to 0.1 of its previous value? *Ans.* 0.04211 mole.

173. What difference would be observed if this had been a dibasic organic acid with the same constant?

174. A small amount of a base is mixed with a large amount of a solution containing equi-molecular amounts of acetic and lactic acids. In what proportion will they form salts? *Ans.* Acetic:lactic::0.00424:0.0117.

175. What solution of glycollic acid ($K = 15.2 \times 10^{-5}$) is isohydric with a 0.1 molar solution of acetic acid ($K = 1.8 \times 10^{-5}$)? *Ans.* $V = 84.4$ liters or 0.01184 molar.

176. A small amount of base is mixed with a large amount of an equimolecular mixture of two acids. The ionization of one is 10%, of the other 90%. How much of each salt will be present in 100 parts of the salt formed?

177. A mixture of glutaric acid with NaOH required after distribution between water and ether, 10.7 cc. of 0.0972 normal $Ba(OH)_2$ for 20 cc. of the water layer, and 18.6 cc. of $0.00992N$ $Ba(OH)_2$ for 50 cc. of the ether layer The coefficient of partition of the glutaric acid between water and ether is 3.58; the dissociation of the neutral sodium salt is 79%, while that of the acid salt is 70%; the equilibrium constant for the first hydrogen

of glutaric acid is $.47 \times 10^{-6}$ and the total sodium present is 0.0928. Find the equilibrium constant for the second hydrogen. *Ans.* 6.3×10^{-6}.

178. The constant for the first hydrogen of malonic acid is 158×10^{-5}, of the second is $1. \times 10^{-6}$. What is the concentration of H· ion in a solution of 1 mole of malonic acid in 2000 liters?

Ans. 0.8385, i.e., $c_{HA'} = 0.7985$.

179. The degree of ionization α for KCl is 0.71667 for $V = 1$, 0.90524 for $V = 32$, 0.9134 for $V = 64$. Calculate K by the dilution laws of Ostwald, Rudolphi, and van't Hoff.

180. The value of K for a 0.05 molar solution of acetic acid is 0.0000175 at 18°, and 0.00001624 at 52°. What is the heat of dissociation of acetic acid? At what temperature would this value be true? *Ans.* 416 cals. at 35°.

181. Find the heat of neutralization of 1 mole of acetic acid (in 200 moles of H_2O) with 1 mole of sodium hydrate (in 200 moles of H_2O) at 35°; α for acetic acid is 0.009, the heat of ionization is 386 cals.; α for NaOH is 0.861, its heat is 1292 cals., and α for sodium acetate is 0.742, its heat being 391 cals. The heat of formation of water from H· and OH′ at 35° is 12,632 cals. *Ans.* 13,093 cals.

182. The solubility of barium sulphate at 37°.7 is 1 mole in 37,283 liters. What is its solubility product t this temperature? *Ans.* 7.2×10^{-10}.

183. PbI_2 is soluble to 0.00158 mole per liter at 25°.2; e.,

$$c_{Pb''} \times c_{I'}^2 = s.$$

What is its solubility in presence of a 0.1 molar solution of I' ions? *Ans.* 1.58×10^{-6} moles per liter.

184. Water under atmospheric pressure at 16° absorbs 0.9753 liters of CO_2 to the liter, i.e., 0.04354 moles per liter. Of this 0.000115 mole is ionized (0.264%) into $H^{\cdot}$ and HCO_3' ions. What is the solubility product of H_2CO_3? *Ans.* 1.32×10^{-8}.

185. At 25° solubility product of H_2CO_3 into $H^{\cdot}$ and HCO_3' is 1.32×10^{-8}. Find concentration of $H^{\cdot}$ and HCO_3' ions.

186. The solubility product of the substance AC_2 is 0.00621. Find concentration of A and C ions when the substance ionized completely into $A^{\cdot\cdot}$ and $2C'$.

Ans. 0.1157 mole per liter of $A^{\cdot\cdot}$ and 0 2314 of C''..

187. AgCNO is soluble at 100° to 0.008 mole per liter. How much would dissolve in a solution containing 0.1 mole of Ag ions?

Ans. $= 6.4 \times 10^{-4}$ moles per liter.

188. The solubility of a salt is 0.0001 mole per liter The formula of the base is $M(OH)_4$, and its solubility is 0.00001, ionizing into $M^{::}$ and $4OH'$. Will it dissociate hydrolytically in water at 25°, for which $K = (0.91 \times 10^{-7})^2$?

Ans. No.

189. At a dilution of 32 liters a binary substance is 0.9% hydrolyzed. What is the percentage of hydrolysis at 100 liters? *Ans.* 1.584%.

190. The solubility of $Mg(OH)_2$ is 0.00002 mole per liter. If there are 1.5 moles of $NH_4^{\cdot}$ as NH_4Cl and 0.0001 of a mole of $Mg^{\cdot\cdot}$ ion present in a molar solution of NH_4OH, what concentrations of OH' ion must be added before the solubility product of $Mg(OH)_2$ can be reached? K for $NH_4OH = 0.000023$. *Ans.* 0.26×10^{-5}.

191. Aniline distributes between water and ether so that there is always 10.1 times as much in the ether as in water. Starting with 0.03138 mole per liter of aniline hydrochloride, and shaking this liter of water solution with 59 cc. of ether we find 0.02916 gram of aniline in 50 cc. of the ether layer. Find the hydrolytic dissociation of aniline hydrochloride in the water solution.

Ans. 2.5%.

192. The constant of hydrolytic dissociation at 100° for NH_4Cl is $337 \times 10^{-10}\left(\text{i.e., } K = \frac{\alpha^2}{(1-\alpha)V} \cdot \frac{d_a}{d_s}\right)$. What is the ionization constant of NH_4OH? $K(H_2O \text{ at } 100^\circ) = (8.5 \times 10^{-7})^2$. *Ans.* 214×10^{-7}.

193. At 25° aniline acetate, $V = 195.9$, is 52.3% hydrolyzed into aniline and acetic acid, both very slightly ionized. The unhydrolyzed salt (V = about 400) is 95.3% ionized. $S_{H_2O} = (1.09 \times 10^{-7})^2$, K for acetic acid is 0.000018. Find the affinity constant of aniline.

Ans. 4.99×10^{-10} (compare with answer to Problem 199.)

194. At 25° the solubility of AgBr is 86×10^{-8}, and of

AgI is 0.97×10^{-8}. How much Br′ in the ionic state must be added to start precipitation of AgBr from solution of AgI? *Ans.* 7.63×10^{-5}.

195. AgCl, AgBr, and AgI are dissolved together. What concentration exists of $Ag^{\cdot}$, Br′, Cl′, and I′ ions per liter? The solubility of AgCl is 1.25×10^{-5}, the others are given above.

196. Brom-iso-cinnamic acid at 25° is soluble to 0.0176 mole per liter, and is ionized to the extent of 1.76% into $H^{\cdot}$ and a negative ion. What is the solubility product of the acid? *Ans.* 9.6×10^{-8}.

197. How much of this acid must always remain in solution at 25°, even in the presence of an infinite amount of $H^{\cdot}$ ions from another acid?

Ans. 0.0173 mole per liter.

198. What is the *solubility* of brom-iso-cinnamic acid in the presence of a 0.001 molar solution of $H^{\cdot}$ ion from another acid?

Ans. Solubility $= 0.0173 + 0.0000883$ mole per liter.

199. K for cinnamic acid at 25° is 0.0000345, and its solubility in water is 0.00331 mole per liter, the ionization being 9.84%. In a 0.01 molar solution of aniline the solubility is increased to 0.00804 mole per liter. The salt formed is ionized at this dilution to 93% and s_{H_2O} is $(1.09 \times 10^{-7})^2$. What is the constant $\left(K = \dfrac{c_{M^{\cdot}} c_{OH'}}{c_{MOH}}\right)$ for aniline? *Ans.* 5.3×10^{-10}.

ELECTROCHEMISTRY.

200. Change 1000 calories into watt-seconds.

Ans. 4178.

201. Change 350 watt-seconds into calories.

Ans. 83.8.

202. An aqueous solution of $CuSO_4$ is electrolyzed until 0.2955 gram of Cu are deposited, using inert electrodes. The liquid at the cathode before passage of the current gave 2.2762 grams Cu, and after passage 2.0650 grams. Find the mobilities of $Cu^{\cdot\cdot}$ and SO_4''.

Ans. $U_{Cu^{\cdot\cdot}} = 0.285$, $U_{SO_4''} = 0.715$.

203. An aqueous solution of $CuSO_4$ is electrolyzed with Cu electrodes until 0.2294 gram of Cu is deposited. Before electrolysis the solution at the anode contained 1.195 grams Cu, after electrolysis 1.360 grams. Find mobilities of $Cu^{\cdot\cdot}$ and SO_4''.

Ans. $U_{Cu^{\cdot\cdot}} = 0.28$, $U_{SO_4''} = 0.72$.

204. A 0.02 molar solution of KCl ($\kappa_{18^\circ} = 0.002397$) gives in a certain electrolytic cell a resistance of 150 ohms. Find factor which will transform conductivity results for this cell into specific conductivities.

Ans. 0.36.

205. Find the ionization constant for NH_4OH. $\Lambda_8 = 3.4$, $\Lambda_{16} = 4.8$, $\Lambda_{32} = 6.7$, $\Lambda_{64} = 9.5$, $\Lambda_{128} = 13.5$ and $\Lambda_{256} = 18.2$. Λ_∞ for NH_4Cl is 130.1, Λ_∞ for KOH is 239.3, and Λ_∞ for KCl is 131.2. *Ans.* K (average) $= 0.000026$.

206. At 18° lactic acid gives the following values:

$\Lambda_{32}=23.11$, $\Lambda_{64}=32.21$, $\Lambda_{128}=44.47$, $\Lambda_{256}=60.23$, $\Lambda_{572}=82.2$, and $\Lambda_{1024}=116.9$. What is the ionization constant? Λ_∞ for HCl is 383.9, Λ_∞ for NaCl is 111, and Λ_∞ for the sodium salt of lactic acid is 85.1.

Ans. K (average) $=0.000136$.

207. In a 0.01 molar solution of KNO_3, NO_3' has a mobility of 0.497, and $K^\cdot$ one of 0.503. Find the equivalent conductivity of NO_3' and $K^\cdot$ in this solution, $\kappa=0.001044$. *Ans.* $l_{K^\cdot}=52.5$, $l_{NO_3'}=51.9$.

208. At infinite dilution the equivalent conductivity of a solution is 91. What would it be at a dilution at which it is 50% dissociated into 2 ions? *Ans.* 45.5.

209. For hydriodic acid we have the following data: $\Lambda_2=364$, $\Lambda_4=376$, $\Lambda_8=384$, $\Lambda_{16}=391$, $\Lambda_{32}=397$, $\Lambda_{34}=402$, $\Lambda_{128}=405$, and $\Lambda_{256}=406$. Compare the constancy of the Ostwald and van't Hoff dilution laws. $l_{\infty H^\cdot}=318$, $l_{\infty I'}=66.7$.

210. The velocity of migration of $Ag^\cdot$ is 0.00057 cm. per second, as is also that of ClO_3'. What is the equivalent conductivity of a solution of $AgClO_3$ which is infinitely dilute? *Ans.* 110.

211. The equivalent conductivity of the sodium salt of an acid is $\Lambda_{32}=89.9$, $\Lambda_{64}=97.1$, $\Lambda_{128}=104.5$, $\Lambda_{256}=111.1$, $\Lambda_{512}=117.2$, and $\Lambda_{1024}=122.7$. What is the basicity of the acid?

212. The equivalent conductivity of a solution of Na_2SO_4 in 100 liters at 25° is 134.9. What is it at infinite dilution? *Ans.* 153.9.

213. The conductivity of a solution of AgCl saturated at 18° is 2.4×10^{-6}; that of the water used is 1.16×10^{-6}. What is the solubility of AgCl? $\Lambda_{\infty \mathrm{KCl}} = 131.2$, $\Lambda_{\infty \mathrm{AgNO_3}} = 116.5$, and $\Lambda_{\infty \mathrm{KNO_3}} = 126.1$.

Ans. 1.02×10^{-5} moles per liter.

214. At 25°, $V = 99.2$, Λ for aniline hydrochloride is 118.6; Λ for aniline hydrochloride plus an excess of aniline is 103.6; Λ_{HCl} ($V = 99.2$) is 411. The conductivity of aniline is negligible. Find the degree of hydrolytic dissociation, and the constant of hydrolytic dissociation. *Ans.* $\alpha = 0.0488$; $K_{\mathrm{hyd.}} = 2.52 \times 10^{-5}$.

215. Find the heat of amalgamation of cadmium at 0°. π for a cell made up of a 1% Cd amalgam and mercury in a solution of $CdSO_4$ is 0.06836 volts at 0°, and 0.0735 at 24°.45.

Ans. $q = 510$ cals. per mole of Cd.

216. Zn in a molar solution of $ZnSO_4$ gives a difference of potential of 0.51 volt and $\frac{\Delta \pi}{\Delta T} = -0.00076$. What is the heat of ionization of Zn at 17°? *Ans.* $337.4K$.

217. $\mathrm{Zn} + 2\mathrm{H}^{\cdot} + 2\mathrm{Cl}' + \mathrm{Aq} = \mathrm{Zn}^{\cdot\cdot} + 2Cl' + \mathrm{Aq} + H_2 + 342K$, and from (216)

$$\mathrm{Zn} = \mathrm{Zn}^{\cdot\cdot} + 337.4K.$$

What is the heat of ionization of H gas?

Ans. $2\mathrm{H}^{\cdot} = H_2 + 5.4K$.

218. A KCN solution is added to the Cu side of a

Daniell cell, and as a result the E.M.F. is zero. What conclusion is to be drawn?

219. A single electrode in connection with the normal electrode ($\pi = 0.56$) gives an E.M.F. of 1.02 volts, the normal electrode being positive. What is the difference of potential between the single electrode and its solution? *Ans.* 0.46 volt, metal is negative.

220. A cell with electrodes of the same univalent metal gives an E.M.F. at 17° of 0.35 volt. The concentration of metal ions at the positive electrodes is 0.02 mole per liter. What is the ionic concentration on the other side? *Ans.* 1.637×10^{-8} moles per liter.

221. Find the E.M.F. of the cell at 25°. H gas – KOH $n/10 (\alpha = 0.85)$ – HCl $n/1 (\alpha = 0.7)$ H gas. $S_{H_2O} = (1.09 \times 10^{-7})^2$. *Ans.* 0.757 volts.

222. Find concentration of OH′ ion in the base. The cell, H gas – base – $n/1$ HCl ($\alpha = 0.7$) H gas, gives 0.8 volt at 25°. $S_{H_2O} = (1.09 \times 10^{-7})^2$.

Ans. $c_{H^\cdot} = 2.6 \times 10^{-14}$.

$c_{OH'} = 0.457$.

223. With a cell with electrodes of a divalent metal, with the ionic concentrations on the two sides equal to 0.02 and 1.62×10^{-8} moles per liter, what would the E.M.F. at 17° have been? *Ans.* 0.175 volt.

224. In a hydrogen gas cell there is acetic acid on one side and propionic on the other of the same con-

centration; what is the E.M.F. of the cell at 17°, and which pole is positive?

Ans. Acetic acid positive, $\pi = 0.00369$ volt.

225. In the above cell the pressure of hydrogen gas is increased to ten times its value on both electrodes. How does the E.M.F. change?

226. What increase in E.M.F. is necessary to separate up to 0.0001 mole of a univalent metal over that which has separated 0.01 mole per liter, the temperature is 17°? *Ans.* 0.115 volt.

227. Assume in 188 that the metal is divalent. What would be the E.M.F. then? *Ans.* 0.0575 volt.

TABLES.

DEGREE OF IONIZATION ACCORDING TO CONDUCTIVITY MEASUREMENTS.

HCl

V	$\alpha_{0°}$	$\alpha_{15°}$	$\alpha_{25°}$	$\alpha_{35°}$
2	0.899	0.874	0.876	0.863
8	0.948	0.937	0.942	0.941
16	0.959	0.946	0.962	0.965
32	0.971	0.980	0.980	0.977
128	0.993	0.999	1.000	1.000
512	1.000	1.000	1.000	1.000

HNO_3.

V	$\alpha_{0°}$	$\alpha_{18°}$	$\alpha_{25°}$	$\alpha_{35°}$
2	0.906	0.883	0.879	0.879
8	0.952	0,951	0.952	0.950
16	0.982	0.975	0.978	0.974
32	0.985	0.988	0.992	.....
128	0.995	0.999	0.993	1.000
512	0.992	0.999	0.995	0.999
1024	1.000	1.000	1.000	1.000

H_2SO_4.

V	$\alpha_{0°}$	$\alpha_{15°}$	$\alpha_{25°}$	$\alpha_{35°}$
2	0.555	0.532	0.547	0.542
8	0.612	0.602	0.597	0.572
16	0.643	0.631	0.631	0.625
32	0.702	0.685	0.687	0.690
128	0.801	0.782	0.817	0.800
512	0.900	0.879	0.947	0.888
1024	0.950	0.969	0.977	0.984
2048	0.977	0.990	0.989	0.996
4096	0.986	1.000	1.000	0.998
8102	0.990	1.000	1.000	1.000

DEGREE OF IONIZATION ACCORDING TO CONDUCTIVITY MEASUREMENTS—*Continued.*

KOH.

V	$\alpha_{0°}$	$\alpha_{18°}$	$\alpha_{25°}$	$\alpha_{35°}$
1	0.847	0.803	0.819	0.833
2	0.884	0.860	0.876	0.883
8	0.916	0.907	0.892	0.900
16	0.936	0.935	0.938	0.959
32	0.952	0.958	0.987	0.996
128	0.998	0.993	1.000	1.000
256	1.000	1.000	1.000	1.000

NaOH.

1	0.780	0.782	0.766	0.774
2	0.838	0.867	0.835	0.843
8	0.920	0.904	0.920	0.935
16	0.936	0.925	0.944	0.951
32	0.971	0.957	0.968	1.000
128	0.992	0.995	1.000	0.989
256	1.000	1.000	1.000	0.981

KBr.

V	$\alpha_{0°}$	$\alpha_{18°}$	$\alpha_{25°}$	$\alpha_{30°}$	$\alpha_{35°}$
2	0.788	0.793	0.789	0.768	0.747
8	0.823	0.849	0.840	0.828	0.821
16	0.872	0.881	0.876	0.867	0.862
32	0.892	0.921	0.900	0.884	0.885
128	0.920	0.961	0.955	0.938	0.926
512	0.949	0.984	0.983	0.987	0.985
1024	1.000	1.000	1.000	1.000	1.000

KI.

V	$\alpha_{0°}$	$\alpha_{18°}$	$\alpha_{25°}$	$\alpha_{35°}$
1	0.767	0.777	0.767	0.760
2	0.800	0.817	0.791	0.792
8	0.850	0.859	0.852	0.854
16	0.905	0.886	0.872	0.881
32	0.935	0.940	0.914	0.930
128	0.979	0.961	0.959	0.954
512	1.000	0.983	0.993	0.996
1024	1.000	0.999	1.000	0.996

DEGREE OF IONIZATION ACCORDING TO CONDUCTIVITY MEASUREMENTS.—*Continued.*

K_2SO_4.

2	0.542	0.539	0.546	0.532
8	0.648	0.647	0.658	0.662
16	0.709	0.706	0.711	0.714
32	0.766	0.740	0.750	0.771
128	0.863	0.852	0.893	0.893
512	0.924	0.938	0.965	0.949
1024	0.985	0.986	0.994	0.989
2048	1.000	1.000	1.000	1.000

MOLECULAR SURFACE TENSION.

T	$x(Mv)^{\frac{2}{3}}$	T	$x(Mv)^{\frac{2}{3}}$	T	$x(Mv)^{\frac{2}{3}}$
		HCl.			
163.1	263.7	175.8	244.8	187.2	229.3
168.5	255.9	180.1	239.0	189.9	223.6
171.8	250.8	183.2	233.6	192.6	221.0
		HBr.			
181.9	330.1	188.9	314.6	198.2	294.8
184.8	325.6	193.4	307.3	200.5	292.2
186.1	320.1	195.3	299.6	203.9	283.8
		HI.			
225.3	367.0	230.9	355.3	235.0	348.0
227.1	362.8	232.9	351.0	236.5	344.6
229.3	358.5	.....	.....	.....	.....
		H_2S.			
189.1	349.5	197.4	334.1	203.9	324.7
191.3	345.3	199.7	328.3	206.9	316.7
194.6	338.0	201.5	326.6	210.8	308.6
		PH_3.			
167.1	287.2	175.4	273.4	.....	.....
171.8	279.6	179.9	265.4	.....	.....

VARIATION OF MOLECULAR SURFACE TENSION WITH THE TEMPERATURE, AND FACTOR OF ASSOCIATION.

	HCl	HBr	HI	H_2S	PH_3
$\frac{\Delta[x(Mv)^{\frac{2}{3}}]}{\Delta T}$	1.47	2.03	1.99	1.91	1.70
y.......	1.5	1.0	1.0	1.1	1.4

DATA FOR DIFFICULTL

(Böttger, Zeit. f. phy

Salt.	t.	Conductivity ×106 less that of H_2O.	l_a+l_c i.e. Λ_∞.	Ionic Concentratio Equivalents per Lite
$CaSO_4$	19.94	19.68	125.9	1.56×10^{-2}
AgCl	19.95	1.33	125.5	1.06×10^{-5}
AgBr	19.96	0.057	127.1	$4.5\ \times10^{-7}$
AgSCN	19.96	0.096	116.1	$8.2\ \times10^{-7}$
AgCN	19.96	0.19	115.5	$1.6\ \times10^{-6}$
$AgBrO_3$	19.94	663.9	105.3	6.30×10^{-3}
$AgIO_3$	19.95	14.05	92.5	1.51×10^{-4}
Ag_2O	19.96	29.27	237.2	1.23×10^{-4}
Ag_2O	24.96	35.98	259.1	1.38×10^{-4}
$Ag_2C_2O_4$	19.96	28.76	123.7	2.32×10^{-4}
Ag_3PO_4	19.46	6.10	135.0	$4.5\ \times10^{-5}$
Ag_2S	25.0	....	....	....
TiCl	19.96	168.0	137.3	1.22×10^{-2}
TlBr	20.06	220.9	138.9	1.59×10^{-3}
TlI	20.15	26.18	138.0	1.89×10^{-4}
TlSCN	19.94	140.0	127.9	1.09×10^{-2}
$TlBrO_3$	19.94	108.0	117.1	9.22×10^{-3}
$TlIO_3$	19.95	154.2	104.3	1.47×10^{-3}
$Tl_2C_2O_4$	19.96	534.4	135.5	3.94×10^{-2}
Tl_2S	19.96	216.0	.....	....
$PbCl_2$	19.95	5354	133	$Pb^{\cdot\cdot}$ 0.0168 $PbCl'$. 0.0109 Cl' 0.0444 $PbCl_2$ 0.00127
$PbBr_2$	19.96	3692	134.6	$Pb^{\cdot\cdot}$ 0.0106 $PbBr'$ 0.0110 Br' 0.0322 $PbBr_2$ 0.00114
PbI_2	20.10	338.4	133.7	2.53×10^{-3}
$Pb(SCN)_2$	19.96	2640	123.6	$Pb^{\cdot\cdot}$ 0.0121 $PbSCN'$ 0.00727 CNS' 0.00315 $Pb(SCN)_2$ 0.000615
$Pb(BrO_3)_2$	19.94	4635	112.8	4.11×10^{-2}
PbO	19.96	25.5	244.7	1.04×10^{-4}
$PbCO_3$	19.96	1.5	127.5	$1.2\ \times10^{-5}$
PbC_2O_4	19.96	1.52	131.2	1.16×10^{-5}
$PbSO_4$	24.95	40.19	151.2	2.65×10^{-4}
$Pb_3(PO_4)_2$	19.95	0.14	142.5	$9.8\ \times10^{-7}$

SOLUBLE SALTS.

Chem., 46, 521, 1903.)

Solubility Product (Moles).	Total Concentration in Equivalents.	α	Grams per Liter.	1 Gram in *x* cc. *x*
2.44×10^{-4}	2.99×10^{-2}	0.524	2.03	491.1
1.12×10^{-10}	1.06×10^{-5}	1.000	1.53×10^{-3}	653600
2.0×10^{-13}	4.5×10^{-7}	1.000	0.84×10^{-4}	11900000
6.8×10^{-13}	8.2×10^{-10}	1.000	1.3×10^{-4}	7300000
2.6×10^{-12}	1.6×10^{-6}	1.000	2.2×10^{-4}	4540000
3.97×10^{-5}	6.7×10^{-3}	0.943	1.58×10^{-4}	538.8
2.31×10^{-8}	1.54×10^{-4}	0.994	4.35×10^{-2}	22970
1.52×10^{-8}	1.84×10^{-4}	0.668	2.14×10^{-2}	46700
1.93×10^{-8}	2.16×10^{-4}	0.643	2.50×10^{-2}	40000
6.29×10^{-12}	2.40×10^{-4}	0.977	3.65×10^{-2}	27390
1.3×10^{-18}	4.6×10^{-5}	0.98	0.64×10^{-2}	155000
2.28×10^{-51}	....	....	....	....
1.50×10^{-4}	1.35×10^{-2}	0.90	3.25×10^{-2}	307.1
2.53×10^{-6}	1.64×10^{-3}	0.968	0.476×10^{-2}	2101
3.60×10^{-8}	1.92×10^{-4}	0.989	0.636×10^{-1}	15720
1.19×10^{-4}	1.20×10^{-2}	0.906	3.15×10^{-1}	317.1
8.50×10^{-5}	9.94×10^{-3}	0.927	3.46×10^{-1}	288.7
2.19×10^{-6}	1.52×10^{-3}	0.971	0.578×10^{-1}	1730
3.06×10^{-5}	6.35×10^{-2}	0.62	15.77×10^{-1}	63.4
....	0.86×10^{-3}	.....	0.21×10^{-1}	4650
....	6.92×10^{-2}	0.044 undiss. $PbCl_2$	9.61×10^{-1}	104
....	4.54×10^{-2}	0.05 undiss. $PbBr_2$	8.34×10^{-1}	119
8.10×10^{-7}	2.61×10^{-3}	0.97	0.470×10^{-1}	2127
....	2.78×10^{-2}	0.044 undiss. $Pb(SCN)_2$	4.50×10^{-1}	222.0
3.47×10^{-5}	5.78×10^{-2}	0.72	13.37×10^{-1}	74.78
....	1.53×10^{-4}	0.68	1.71×10^{-2}	58600
0.36×10^{-10}	1.2×10^{-5}	0.96	1.6×10^{-3}	595000
0.338×10^{-10}	1.22×10^{-5}	0.95	1.80×10^{-3}	556000
1.76×10^{-8}	2.88×10^{-4}	0.92	4.38×10^{-2}	22830
1.2×10^{-32}	1.0×10^{-6}	0.98	1.3×10^{-4}	7400000

SOLUBILITY OF SILVER SALTS.

(Moles per liter.)

Chloracetate	17°	6.4×10^{-2}	Valerate	18°	9.5×10^{-3}
Borate	25°	6×10^{-2}	Benzoate	14°.5	7.7×10^{-3}
Acetate	18°.6	5.9×10^{-2}	Salicylate	15°	3.9×10^{-4}
Propionate	18°	4.6×10^{-2}	Chromate	18°	1.7×10^{-4}
Sulphate	18°	2.33×10^{-2}	Carbonate	25°	1.2×10^{-4}
	25°	2.57×10^{-2}	Sulphide	18°	4×10^{-11}
Butyrate	18°	2.23×10^{-2}			

SOLUBILITY PRODUCTS.

(Moles per liter.)

Sub.	t	Solubility.	Conc. of Ions.	s
$Hg_2(SCN)_2$	25°	1.7×10^{-7}	....	1.8×10^{-20}
Hg_2I_2	25°	2.5×10^{-10}	$Hg_2^{\cdot\cdot} = 3 \times 10^{-10}$	1.2×10^{-28}
Hg_2Br_2	25°	5.6×10^{-8}	$Hg_2^{\cdot\cdot} = 7 \times 10^{-8}$	1.3×10^{-21}
Hg_2Cl_2	25°	0.8×10^{-6}	$Hg_2^{\cdot\cdot} = 1 \times 10^{-6}$	3.5×10^{-18}
$HgCl_2$	25°	0.262	$Hg^{\cdot\cdot} = 9 \times 10^{-6}$	2.6×10^{-15}
$HgBr_2$	25°	....	$Hg^{\cdot\cdot} = 27 \times 10^{-8}$	8×10^{-20}
HgI_2	25°	....	$Hg^{\cdot\cdot} = 2 \times 10^{-10}$	3.2×10^{-29}
$Hg(OH)_2$	17°	....	....	1.5×10^{-26}
$Zn(OH)_2$	17°	....	....	4.8×10^{-1}
$Ni(OH)_2$	17°	....	....	2.1×10^{-2}
$Co(OH)_2$	17°	....	....	5.4×10^{-3}
$Cd(OH)_2$	17°	....	....	2.7×10^{-3}

SOLUBILITIES AT 18°.

	$\kappa_{18} \times 10^6$	Mg. Eq. per Liter.
BaF_2	1530	18.4
SrF_2	172	1.87
CaF_2	40	0.42
MgF_2	224	2.8
PbF_2	431	5.2
$BaSO_4$	2.4	0.020
$SrSO_4$	127	1.24
$BaCrO_4$	3.2	0.03
$PbCrO_4$	0.1	0.001
$BaC_2O_4 \cdot 2H_2O$	78.3	0.76
SrC_2O_4	54	0.52
$CaC_2O_4 \cdot 2H_2O$	9.6	0.087
$MgC_2O_4 \cdot 2H_2O$	200	5.36
$ZnC_2O_4 \cdot 2H_2O$	8.0	0.083
$CdC_2O_4 \cdot 3H_2O$	27.0	0.33

ELECTRICAL CONDUCTIVITY (MOLECULAR)

Solvent.	Salt.	Specific Conductivity of Solvent.
Allylalcohol	$FeCl_3$	6.5×10^{-6}
Benzylalcohol	$FeCl_3$	1.8×10^{-6}
Paraldehyde	$FeCl_3$	$< 3.4 \times 10^{-7}$
"	$SbCl_3$	....
Salicylaldehyde	$FeCl_3$	6.0×10^{-6}
Furfurol	$FeCl_3$	2.4×10^{-5}
Methylpropylketone	$FeCl_3$	9.5×10^{-7}
Acetophenone	$FeCl_3$	1.8×10^{-7}
Ethylmonochloracetate	$FeCl_3$	$< 1.7 \times 10^{-6}$
"	$SbCl_3$	....
"	$CuCl_2$	....
Ethylcyanacetate	$FeCl_3$	3.7×10^{-7}
"	$AgNO_3$	....
"	$CuCl_2$	....
Ethyloxalate	$FeCl_3$	7.1×10^{-7}
Ethylbenzoate	$FeCl_3$	1.8×10^{-7}
Amylnitrate	$FeCl_3$	1.8×10^{-7}
Nitrobenzol	$BiCl_3$	$< 3.5 \times 10^{-7}$
"	$AlCl_3$	....
Orthonitrotoluol	$FeCl_3$	$< 1.8 \times 10^{-7}$
"	$SbCl_3$	....
Metanitrotoluol	$FeCl_3$	$< 1.8 \times 10^{-7}$
Benzonitril	$AgNO_3$	1.9×10^{-6}
Pyridine	$FeCl_3$	7.5×10^{-7}
"	$AgNO_3$	....
"	$AgCN$	....
"	$Pb(NO_3)_2$	....
"	$CuCl_2$	....
"	$Hg(CN)_2$	....
"	HgI_2	....
"	$Ag_2C_6H_4O_6$	....
"	$CoCl_2$	....
Piperidine	$AgNO_3$	$< 1.8 \times 10^{-7}$
Chinoline	$AgNO_3$	3.7×10^{-7}

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* See Lincoln. J. phys.

IN NON-AQUEOUS SOLVENTS, 25°.*

V	μ	*V*	μ	*V*	μ	*V*	μ
20.02	17.42	53.71	23.03	115.6	32.15	....	....
88.06	2.62	895.22	6.31	....	....	....	....
4.37	9.81	42.52	18.76	183.11	16.51	575.5	16.91
5.57	0.202	20.76	0.356	61.16	0.522	....	....
20.4	3.76	81.38	4.71	220.74	5.6	....	....
45.6	20.78	80.98	22.2	149.21	26.42	....	....
13.64	28.25	22.83	31.07	53.36	36.98	100.71	42.76
23.46	10.28	65.77	11.59	124.91	12.03	292.98	13.08
7.76	12.45	22.09	13.75	92.05	16.38	152.55	17.88
4.25	0.174	11.49	0.201	44.73	0.337	....	....
13.32	1.24	....	....	....	....	....	....
15.3	8.88	27.08	9.29	44.64	9.8	185.22	11.57
10.62	4.19	28.3	5.29	58.57	6.46	110.97	7.66
29.85	7.00	41.67	7.5	59.4	8.08	97.77	12.8
13.15	5.88	42.29	5.92	94.79	6.25	342.85	7.7
29.45	1.55	174.28	1.61	517.21	1.91	....	....
21.34	1.54	38.74	1.74	264.16	3.00	644.56	3.73
8.5	0.8	34.02	0.96	136.07	1.07	272.14	1.11
4.69	3.67	9.38	4.51	....	....	....	....
10.94	8.37	25.99	10.74	74.28	13.32	201.43	15.24
3.4	0.056	6.55	0.088	19.82	0.244	39.10	0.39
10.86	6.86	84.77	12.55	448.14	19.00	814.8	18.2
2.1	3.37	16.3	5.2	24.1	7.66	44.62	10.12
6.1	7.96	24.58	6.85	93.7	5.9	159.55	5.57
7.55	24.1	51.43	29.5	392.3	40.16	784.6	45.21
14.64	4.78	38.4	5.42	100.47	6.16	393.0	6.47
21.1	0.81	55.96	1.57	168.5	3.25	....	....
45.1	0.98	57.04	1.16	....	....	....	....
5.35	0.012	13.1	0.014	357.4	0.53	....	....
21.8	0.35	93.6	1.4	200.1	2.7	....	....
340.7	14.64	1505.9	35.3	....	....	....	....
74.06	0.2	805.3	1.45	....	....	....	....
4.24	0.368	7.88	0.154	10.5	0.091	15.6	0.043
4.8	2.45	9.6	2.79	34.9	2.8	129.8	3.62

Chem., 3, 457, 1899.

SOLUBILITY OF GASES IN WATER AT 0°, 760 MM.

VOLUMES OF GAS IN ONE VOLUME OF WATER.

H =0.0193
N =0.02035
O =0.04114
NO=1.3052

CO_2= 1.7967
H_2S = 4.3706
SO_2 = 79.789
NH_3=1148.8

LIQUEFACTION OF GASES.

Pressures in atmospheres at 0°.

SO_2 = 1.53
CN = 2.37
HI = 3.97
NH_3= 4.4
Cl = 4
H_2S =10
NO =32
CO_2=35.4
HCl =about 42

Temperatures at atmos. pressure.

SO_2 = −10°
CN = −22
NH_3= −36
Cl = −50
CO_2= −87

DIELECTRIC CONSTANTS AT 20°.

Water, H_2O	81.12	Pyridine, C_5H_5N	ab. 20
Formic acid, HCOOH	57	Piperidine, $C_5H_{10}NH$	>20
Nitromethane, CH_3NO_2	56.4	Acetylchloride, CH_3COCl	15.4
Acetonitrile, CH_3CN	ab. 40	Methyliodide, CH_3I	7.2
Methylalcohol, CH_3OH	32.5	Ethylacetate, $CH_3COOC_2H_5$	5.8
Propionitrile, CH_3CH_2CN	ab. 30	Chloroform, $CHCl_3$	5.2
Ethylalcohol, C_2H_5OH	26.8	Ether, $(C_2H_5)_2O$	4.36
Acetaldehyde, CH_3COH	21.1	Benzene, C_6H_6	2.29
Acetone, CH_3COCH_3	20.7	Toluol, $C_6H_5CH_3$	2.31
Glycerine,		Aniline, $C_6H_5NH_2$	7.31
$CH_2OH.CHOH.CH_2OH$	16.5	Chinolin, C_9H_7N	8.9
Ethylnitrate, $C_2H_5ONO_2$	19.6	Benzylcyanide, $C_6H_5CH_2CN$	15
NH_3	16.2	Benzonitrile, C_6H_5CN	26
SO_2	13.75	Nitrobenzene, $C_6H_5NO_2$	36.45

DEPRESSION OF THE FREEZING-POINT, $K_{f.p.}$.

Solvent.	$K_{f.p.}$ **(1 mole in 1000 grams).**
Benzene	4.9
Phenol	7.4
Water	1.86
Acetic acid	3.9
Nitrobenzene	7.05

INCREASE OF THE BOILING-POINT, $K_{b.p.}$.

Solvent.	$K_{b.p.}$ **(1 mole in 1000 grams).**
Water	0.52
Carbon tetrachloride	4.8
Chloroform	3.66
Methyl alcohol	0.88
Ethyl alcohol	1.15
Ether	2.11
Acetone	1.67
Benzene	2.67
Aniline	3.22
Phenol	3.04

LOGARITHMS.

Proportional Parts.

Nat. numb.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	6	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7

LOGARITHMS—*Continued.*

Proportional Parts.

Nat. numb.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
[illegible]	[illegible]031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	0484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
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